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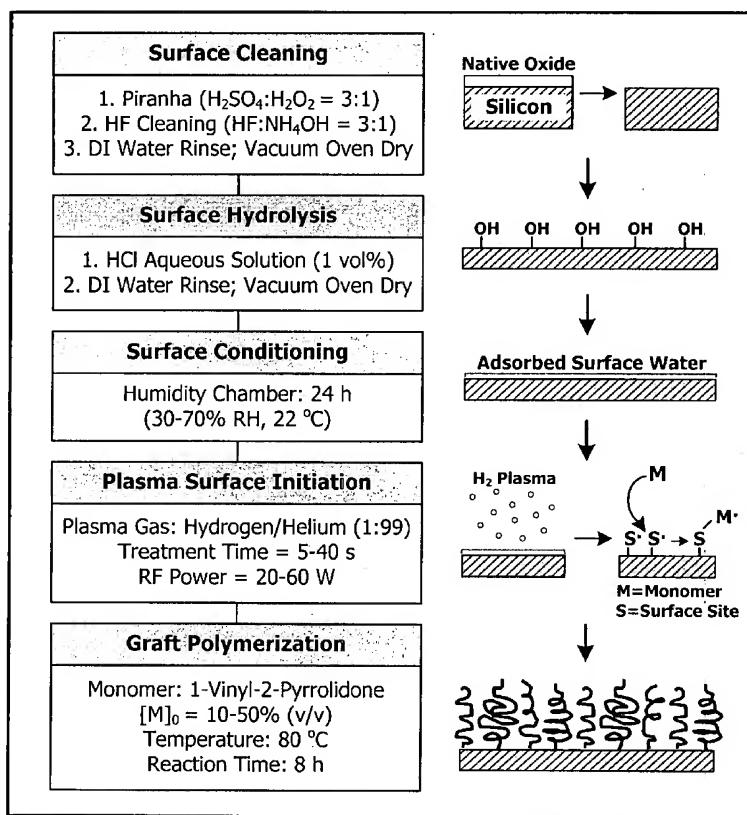
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[Continued on next page]

(54) Title: ATMOSPHERIC PRESSURE PLASMA-INDUCED GRAFT POLYMERIZATION



(57) **Abstract:** A method of modifying a polymeric, inorganic, or organic-functionalized substrate surface is provided. In one embodiment, an atmospheric pressure (AP) plasma stream is directed at a substrate surface, leading to the formation of surface-bound active sites that function as polymerization initiators. When contacted with a monomer or monomer solution, the active sites facilitate formation of a dense array of graft polymers covalently bound to the substrate surface. In another embodiment, an inorganic substrate is cleaned, conditioned in a humidity chamber, treated with an AP plasma, and contacted with a monomer or monomer solution to facilitate formation and growth of graft polymers on the substrate surface.

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1 ATMOSPHERIC PRESSURE PLASMA- INDUCED GRAFT POLYMERIZATION

FIELD OF THE INVENTION

[0001] The invention generally relates to surface modification techniques, and more particularly to low temperature, atmospheric pressure plasma surface treatments and graft polymerization processes.

BACKGROUND OF THE INVENTION

[0002] Surface nanostructuring by grafting functional polymers to a substrate surface has been used to enhance chemical functionality and to alter the surface topology of native inorganic and organic materials. For example, graft- polymerized ethylenically unsaturated monomers offers unique properties in applications such as micropatterning in electronics fabrication, adhesion in carbon fibers and rubber dispersions, and as selective layers in fuel cells and separation membranes. Organic and inorganic surfaces modified with grafted polymers have demonstrated anti-fouling characteristics in separation membranes, high chemical selectivity in chemical sensors, and surface lubricating properties. In such applications, the grafted polymer phase, composed of nanoscale, single-molecule chains covalently and terminally bound to a substrate or surrogate surface, serves to impart unique material properties to the substrate while maintaining the chemical and physical integrity of the native surface. Moreover, the grafted chains remain attached to the surface even when exposed to a solvent in which the polymer is completely miscible.

[0003] A tethered polymer phase can be formed either by polymer grafting ("grafting to") or graft polymerization ("grafting from"). Surface chain coverage and spatial uniformity achieved by polymer grafting may be limited by steric hindrance. In contrast, graft polymerization, which is the focus of the present invention, proceeds by sequential monomer addition, thereby allowing for the formation of a denser surface coverage.

[0004] Structuring surfaces with grafted vinyl monomers and other ethylenically unsaturated monomers is commonly achieved by free radical graft polymerization (FRGP), where the polymer chain size, chain length uniformity, and surface density are dictated by the initial monomer concentration, reaction temperature and density of the surface immobilized initiators or initiators in solution. However, broad molecular weight chain size distributions resulting from uncontrolled macroradical reactions in solution and limitations in surface density due to the restriction of pre-grafted surface initiation sites make this approach unattractive for nanoscale-engineered polymer surface architectures.

[0005] Free radical polymerization relies on initiator species to initiate either solution polymerization, in which polymers grown in solution may bind to reactive surface sites by polymer grafting, or surface polymerization, in which monomers undergo direct surface grafting from immobilized surface initiators (e.g., surface-grafted reactive groups) or surface

1 monomers (e.g., ethylenically unsaturated monomers) by graft polymerization (e.g., surface
grafted reactive groups). However, the occurrence of competitive polymer chain grafting,
chain transfer reactions, and surface chain growth by propagation result in a polydisperse
grafted polymer chain size in contrast to the more uniform surface chain size that is achieved
5 by grafting of preformed polymer chains of a uniform size. Further, for inorganic substrates,
the density of grafting sites for graft polymerization is limited by the availability of surface
hydroxyl groups on the oxide surface, which serve as anchoring sites for surrogate surface
initiators and macroinitiators. For example, the surface concentration of hydroxyl groups on
fully hydrolyzed silica and zirconia are 7.6 $\mu\text{moles}/\text{m}^2$ (4.6 molecules/ nm^2) and 5.6-5.9
10 $\mu\text{moles}/\text{m}^2$ (3.4-3.6 molecules/ nm^2), respectively.

[0006] In recent years, the demand for sophisticated, advanced materials for nanoscale devices has led to a growing interest in controlled radical polymerization (CRP), whereby grafted polymer domains may be precisely structured by controlling polymer chain growth and grafted chain polydispersity. CRP utilizes a control agent that reversibly binds to the 15 surface-bound macroradical chain, establishing a thermodynamic equilibrium that favors the capped polymer in the dormant phase. The presence of the control agent limits the number of "live" chains in solution, thus enabling control over the rate of surface polymerization while reducing chain termination. Controlled polystyrene graft polymerization, with number-average molecular weights (M_n) and polydispersity indices (PDI), has been reported for the 20 following CRP methods: atom transfer radical graft polymerization (ATRGP) ($M_n = 10,400$ - $18,000$ g/mol and $PDI = 1.05$ - 1.23), reversible addition-fragmentation chain transfer (RAFT) graft polymerization ($M_n = 12,800$ - $20,000$ g/mol, $PDI = 1.10$ - 1.40), and nitroxide-mediated 25 graft polymerization (NMGP) ($M_n = 20,000$ - $32,000$ g/mol, $PDI = 1.20$ - 1.30) for grafting of polystyrene onto silica and polymeric materials (e.g., polyglycidyl methacrylate (PGMA), polythiophene, polypropylene; and polyacrylate).

[0007] However, ATRGP and RAFT pose unique constraints. For example, ATRP requires a precise initiator-to-catalyst-to-monomer ratio, optimal temperature/solvent conditions, and surface-bound organic halide initiators, which potentially limits the surface graft density. RAFT graft polymerization requires thio-ester surface initiators for grafting. 30 On the other hand, NMGP relies on conventional peroxide initiators and/or thermal initiation to form polymer chain radicals that may then, for example, reversibly bind to an alkoxyamine for controlled polymerization.

[0008] Plasma surface treatment has been proposed as an approach to alter surface chemistry and potentially supplant previous solution phase initiator strategies with high 35 density surface activation. Plasma treatment alone, however, has been shown to be an insufficient surface modification tool; polymeric, plasma-treated surfaces do not retain their modified chemical properties over time and with air exposure. Vapor phase plasma polymerization, in which monomer fed through plasma is initiated in the gas phase and then

1 polymerized on a substrate surface, has also been investigated as a surface modification
method. However, surface-adsorbed radical monomer species, which are designed to
polymerize with condensing monomer radicals from the vapor phase, may in fact be further
modified by continuous plasma bombardment, leading to highly cross-linked, chemically and
5 physically heterogeneous polymer films that are non-covalently adsorbed to the surface.
Also, the local concentration of monomer species in the plasma afterglow is highly dependent
on the radial dimensions of the plasma source, and the resulting spatial variations in
monomer deposition rate may lead to a non-uniform film structure and morphology.

[0009] Plasma-induced graft polymerization (PIGP) is an alternative surface modification
10 approach in which plasma is used to activate the surface, and ethylenically unsaturated
monomers in the liquid phase are sequentially grafted to the initiation sites via a free radical
grafting mechanism. This approach allows one to engineer a grafted polymer phase
characterized by a high surface density of polymer chains that are initiated and polymerized
directly from the substrate surface, thus minimizing polydisperse chain growth, and
15 improving stability under chemical, thermal and shear stresses. Given the complex surface
chemistry and limited lifetime of reactive plasma initiated surface species, the exact chemical
nature of these plasma-generated organic moieties is yet to be established.

[0010] To date, PIGP has focused primarily on low pressure (i.e., below atmospheric)
plasma initiation and surface grafting on polymeric materials. An example is low pressure
20 polystyrene surface grafting used for surface structuring of Nafion fuel cells and separation
membranes. Limited studies of low pressure plasma surface treatment of inorganic oxides,
such as titanium dioxide, have also been reported. However, restrictions associated with low
pressure plasma processing (e.g., the need for a vacuum chamber) are a hindrance for
potential scale-up opportunities in industrial applications.

[0011] A notable limitation for achieving PIGP on inorganic substrates, unlike polymeric
materials, has been the requirement of a sufficiently dense layer of surface activation sites,
created through silylation of reactive monomers or macroinitiator grafting, that may form
surface radicals for polymer initiation upon plasma treatment. Surface preparation required
for such techniques combined with the reliance on surface hydroxyl chemistry limits the
25 large-scale adaptation of such methods and the level of chain density that can be achieved.
Direct plasma initiation and grafting without the use of surrogate surfaces has been
demonstrated qualitatively on titanium oxide particles and silicone rubber materials, with
characteristic surface radical formation noted as a function of treatment time and RF power,
similar to organic materials. Yet, a recent study has demonstrated that, under low pressure
30 plasma surface treatment of Shirasu porous glass, a direct correlation between silanol density
and grafted polymer density is observed. This suggests that the number density of surface
radicals that may be achieved in low pressure plasma surface activation of inorganic oxide
substrates may be limited by the native oxide surface chemistry.

1 [0012] These findings, combined with the added requirement of ultra high vacuum chambers necessary for low pressure plasma processing, indicate that prior art approaches are insufficient for achieving high-density surface activation and graft polymerization, and especially inadequate for large surface area modification of organic and inorganic substrates.

5

SUMMARY OF THE INVENTION

[0013] The present invention provides a novel method of modifying inorganic and organic substrates by growing end-grafted polymers from a surface of the substrate in a controlled manner. In one aspect, the invention comprises treating a substrate surface with (a) an atmospheric pressure (AP) plasma and (b) an ethylenically unsaturated monomer or monomer solution. AP plasma treatment forms "active sites" on the surface that function as surface-anchored polymerization initiators. When contacted with a monomer, the active sites cause the monomer to polymerize, resulting in a plurality of end-grafted polymer chains covalently bound to the substrate. The active sites can be peroxides, oxides, hydroxyls, amines, hydrides, radicals, epoxides, or other chemical moieties, i.e., functional groups capable of initiating polymerization. Polymerization can proceed by classical free radical graft polymerization (FRGP) or controlled radical polymerization (CRP), such as ATRGP, RAFT, NMGP, etc. Surface activation is controlled by adjusting the plasma operating parameters -- e.g., plasma source, plasma precursor and carrier gas, gas flow rate, gas partial pressure, radio frequency power, and applied voltage, as well as surface treatment time and preparation of the substrate surface -- to maximize the formation of surface radicals or peroxides.

[0014] The invention is exemplified by a number of embodiments. For example, for inorganic substrates, one embodiment of the invention comprises the steps of cleaning a surface of a substrate to remove contaminants and a native oxide layer, if present; forming a layer of water on the surface of the substrate by, e.g., placing the substrate in a humidity chamber; generating initiation sites on the substrate surface by treating the substrate with an atmospheric pressure (AP) plasma; and growing polymers from the surface of the substrate by exposing the polymerization initiation sites to a monomer or monomer solution. In another embodiment, the surface of an organic polymeric substrate is modified by generating polymer initiation sites on the substrate surface by treating the substrate with an atmospheric pressure (AP) plasma; and growing polymers from the surface of the substrate by exposing the polymerization initiation sites to an ethylenically unsaturated monomer or monomer solution. In still another embodiment, the method is used to modify the surface of an organo-functionalized inorganic substrate such as a vinyl-functionalized silica or silicon.

[0015] Atmospheric pressure plasma-induced graft polymerization (APPIG polymerization) has a number of advantages over non-plasma, classical free radical graft polymerization and controlled "living" graft polymerization, vapor-phase plasma

1 polymerization, and low-pressure plasma-induced polymerization. Among other things,
APPIG polymerization does not rely on chemical initiators in solution and does not require
expensive -- and potentially scale-up limiting -- ultra-high vacuum chambers and associated
equipment for plasma processing. Initiation of monomer polymerization occurs on the
5 substrate surface, minimizing formation of high molecular weight homopolymers and
polymer grafting from the bulk. Consequently, APPIG polymerization-modified surfaces
exhibit a higher degree of polymer chain length uniformity than classical methods. The
invention also allows a highly dense, substantially uniform layer of single-molecule grafted
10 polymers to be grown sequentially from an inorganic or organic surfaces. Tests on inorganic
substrates, for example, demonstrate that AP plasma treatment directly modifies the inorganic
surface lattice, resulting in a high density of initiation sites that enable graft polymerization
with polymer-polymer separations that can be 10nm or less, without the need for extensive
chemical surface treatment. The invention therefore opens the door to improved materials in
15 a number of fields, such as microelectronics, biomedics, membrane separation, flocculant and
coagulant technology, chemical sensors, and general surface coatings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Various other aspects, embodiments, and advantages of the invention will become
apparent upon reading the Detailed Description and by referring to the appended drawings,
wherein:

[0017] FIG. 1 is a schematic illustration of a method of modifying a silicon substrate
surface according to one embodiment of the invention;

[0018] FIG. 2 is a schematic illustration of an AP plasma generator used in the method
shown in FIG. 1;

[0019] FIG. 3 is a plot showing the effect of plasma treatment time on the presence of
surface radicals (detected using TEMPO binding assay with FTIR analysis) formed by
atmospheric pressure plasma surface treatment (RF power = 40 W, RH = 50% at 22°C)
according to one embodiment of the invention;

[0020] FIG. 4 is a plot showing the effect of plasma radio frequency (RF) power on the
presence of surface radicals (detected using TEMPO binding assay with FTIR analysis)
formed by atmospheric pressure plasma surface treatment (treatment time = 10 sec, RH =
50% at 22°C) according to one embodiment of the invention;.

[0021] FIG. 5 is a plot showing the effect of absorbed surface water coverage on the
presence of surface radicals (detected using TEMPO binding assay with FTIR analysis)
formed by atmospheric pressure plasma surface treatment (treatment time = 10 sec and RF
power = 40 W) according to one embodiment of the invention;.

[0022] FIG. 6 is a pair of tapping mode AFM 3-D surface renderings of native and
poly(vinyl pyrrolidone)-grafted silicon substrate at $[M]_0 = 30\% \text{ (v/v)}$ VP in aqueous solvent

1 with R_{rms} surface roughness and skewness (1x1 μm sample areas) according to one embodiment of the invention;

5 [0023] FIG. 7 is a set of tapping Mode AFM 3-D surface renderings of silicon surfaces graft polymerized with 1-vinyl-2-pyrrolidone in n-methyl-2-pyrrolidone at A) $[M]_0 = 20\%$, B) $[M]_0 = 30\%$, and C) $[M]_0 = 40\%$ (1x1 μm sample areas) according to one embodiment of the invention;

10 [0024] FIG. 8 is a set of tapping mode AFM images of silicon surfaces graft polymerized with 1-vinyl-2-pyrrolidone at $[M]_0 = 30\%$ (v/v) in a mixture of aqueous solvent and A) [NMP] = 15%, B) [NMP] = 40%, C) [NMP] = 60% and D) [NMP] = 100% (no water) (1x1 μm sample areas) according to one embodiment of the invention;

15 [0025] FIG. 9 is a pair of height histograms of 1-vinyl-2-pyrrolidone (PVP)-grafted silicon wafers prepared by graft polymerization of 1-vinyl-2-pyrrolidone at $[M]_0 = 30\%$ (v/v) and solvents A) [NMP] = 60% and B) [NMP] = 100% (treatment time = 10 sec, RF power = 40 W, and RH = 50% at 22°C) according to one embodiment of the invention;

20 [0026] FIG. 10 is a plot showing relative polystyrene film thickness for APPIGP of styrene at initial monomer concentration M10 – M50 at $T = 85^\circ\text{C}$ and $t = 8\text{ h}$ (L_{M30} = film thickness at M30) according to one embodiment of the invention;

25 [0027] FIG. 11 is a plot showing polystyrene film growth rate (i., rate of change of polymer film thickness) versus reaction time for APPIGP at $T = 70^\circ\text{C}$, 85°C , and 100°C : (a) M30, and (b) M50 (surface initiation at treatment time = 10 s, RF power = 40 W, and RH = 50% at 22°C) according to one embodiment of the invention;

30 [0028] FIG. 12 is a plot of graft polystyrene film thickness for rapid initiation at M30 with a step 1 time interval varied between $t = 5$ – 30 min . and a step 2 total reaction time of 3 hours (step 1 = 100°C , step 2 = 85°C) according to one embodiment of the invention;

35 [0029] FIG. 13 is a plot of graft polystyrene film growth for (a) rapid initiation APPIGP (step 1 = 15 min) and (b) APPIGP at M30 and $T = 85^\circ\text{C}$ (surface initiation at treatment time = 10 s, RF power = 40 W, and RH = 50% at 22°C) according to one embodiment of the invention;

40 [0030] FIG. 14 is a set of tapping mode AFM 3-D surface renderings ($1 \times 1 \mu\text{m}^2$) of APPIGP for polystyrene grafted silicon at M30:(a) $T = 70^\circ\text{C}$, (b) $T = 85^\circ\text{C}$, (c) $T = 100^\circ\text{C}$, and at M50: (d) $T = 70^\circ\text{C}$, (e) $T = 85^\circ\text{C}$, (f) $T = 100^\circ\text{C}$, according to one embodiment of the invention;

45 [0031] FIG. 15 is a plot showing experimental polystyrene film growth by nitroxide-mediated APPIGP at M50 and $[\text{TEMPO}] = 5, 7, 10$, and 15 mM (surface initiation at treatment time = 10 s, RF power = 40 W, and RH = 50% at 22°C) according to one embodiment of the invention;

1 [0032] FIG. 16 is a tapping mode AFM 3-D surface rendering ($1 \times 1 \mu\text{m}^2$) of nitroxide-mediated APPGP for polystyrene grafted silicon at M50, T = 120°C, and [TEMPO] = 10 mM according to one embodiment of the invention;

5 [0033] FIG. 17 is a height histogram (with fitted Gaussian distributions) and AFM image (Right) of nitroxide-mediated APPGP for polystyrene grafted silicon at M50, T = 120°C, and [TEMPO] = 10 mM according to one embodiment of the invention.

10 [0034] FIG. 18 is a tapping mode AFM 3-D surface rendering of a silicon surface prior to AP plasma treatment.

[0035] FIG. 19 is a tapping mode AFM 3-D surface rendering of a silylated silicon surface prior to AP plasma treatment.;

15 [0036] FIG. 20 is a tapping mode AFM 3-D surface rendering of an APPIG polymerization-modified silicon surface according to one embodiment of the invention (Ex. 2)(hydrogen plasma, 10s, 40W; 30% (v/v) 1-vinyl-2-pyrrolidone monomer in n-methyl-2-pyrrolidone; T = 80 °C);

20 [0037] FIG. 21 is a tapping mode AFM 3-D surface rendering of an APPIG polymerization-modified silicon surface according to one embodiment of the invention (Ex. 2)(hydrogen plasma, 10s, 40W; 30% (v/v) 1-vinyl-2-pyrrolidone monomer in n-methyl-2-pyrrolidone; T = 90 °C);

25 [0038] FIG. 22 is a tapping mode AFM 3-D surface rendering of an APPIG polymerization-modified silicon surface according to one embodiment of the invention (Ex. 3)(hydrogen plasma, 10s, 40W; 30% (v/v) 1-vinyl-2-pyrrolidone monomer in a 60% (v/v) aqueous mixture of n-methyl-2-pyrrolidone; T = 80 °C);

30 [0039] FIG. 23 is a tapping mode AFM 3-D surface rendering of an APPIG polymerization-modified silylated silicon surface according to one embodiment of the invention (Ex. 4)(hydrogen plasma, 10s, 40W; 30% (v/v) 1-vinyl-2-pyrrolidone monomer in DI water; T = 80 °C);

[0040] FIG. 24 is a tapping mode AFM 3-D surface rendering of an APPIG polymerization-modified polysulfone surface according to one embodiment of the invention (Ex. 6)(hydrogen plasma, 10s, 40W; 30% (v/v) 1-vinyl-2-pyrrolidone monomer in DI water; T = 70 °C); and

35 [0041] FIG. 25 is a tapping mode AFM 3-D surface rendering of an APPIG polymerization-modified silicon surface according to one embodiment of the invention (Ex. 10)(hydrogen plasma, 10s, 40W; 30% (v/v) vinyl acetate monomer in ethyl acetate; T = 70 °C).

35

DETAILED DESCRIPTION

[0042] According to the invention, a novel method of modifying the topology and physico-chemical properties of a substrate surface using APPG polymerization is provided.

1 Generally, the method comprises treating a substrate surface with an atmospheric pressure
2 (AP) plasma and an ethylenically unsaturated monomer or monomer solution. In a preferred
3 approach, an atmospheric pressure plasma stream is directed at the surface, using, for
4 example, an AP plasma jet. AP plasma treatment causes surface-bound active sites, i.e.,
5 chemical functional groups such as peroxides, radicals, etc., to form on the substrate. When
6 contacted with an unsaturated monomer or monomer solution, the active sites (also referred
7 to as polymerization initiators) facilitate the formation and controlled growth of graft
8 polymers from the surface of the substrate. The method is suitable for surface modification
9 of inorganic, organic, and mixed inorganic/organic substrates, such as organo-functionalized
10 substrates, e.g., alkoxy silylated silicon.

[0043] Nonlimiting examples of suitable inorganic substrates include elemental materials,
such as silicon, aluminum, hafnium, zirconium, titanium, iron, and gold; inorganic oxides,
such as silica, alumina, hafnia, zirconia, titania; and other metallic, metalloid, or ceramic
materials capable of supporting the formation of surface oxides, hydroxides, peroxides, or
other functional groups that can initiate polymerization when exposed to a monomer or
monomer solution. In theory, any organic or inorganic substrate capable of supporting the
formation of polymerization initiation sites can be modified using the present invention.
Nonlimiting examples include polymeric materials, dendritic materials, thiols, Langmuir-
Blodgett films, and silylated layers. Specific, nonlimiting examples of organic polymer
substrates include polystyrene, polyamides, polysulfone, poly(vinyl alcohol), and organo-
silicon polymers.

[0044] Figure 1 illustrates a multi-step process of APPIG polymerization according to
one embodiment of the invention in which a silicon wafer is modified by graft polymerizing
1-vinyl-2- pyrrolidone monomers from a surface of the wafer. First, the substrate is prepared
by a multi-step cleaning and conditioning process to remove surface contaminants and the
native oxide layer on the substrate. Thus, the substrate is cleaned in a "piranha" solution
(e.g., 3:1 or 7:3 sulfuric acid : hydrogen peroxide), and then rinsed in deionized water to
remove absorbed organics and acids. Native oxide films present on inorganic silicon are
heterogeneous in nature, can easily be etched, and therefore are removed to ensure effective
graft polymerization. This is accomplished using, e.g., hydrofluoric acid followed by
immersion in a water bath to remove residual acid and the native oxide layer, and then drying
the substrate in a vacuum oven (heated, for example, to a temperature of 60-100°C). Once
dried, the substrate is "conditioned" by placing the substrate in a humidity chamber for
several hours, preferably as long as 24 hours, to ensure that a controlled layer of adsorbed
water is present prior to AP plasma treatment. Alternatively, the surface can be conditioned
in ambient air if the appropriate relative humidity is achieved, although, in general, a
humidity chamber provides better control.

1 [0045] For an inorganic substrate such as silicon, the highest density of surface active sites is obtained when the amount of surface water adsorbed on the substrate surface is carefully controlled prior to AP plasma treatment. Adsorbed water appears to facilitate the formation of peroxides or other surface active groups during plasma treatment, which then act
5 as polymerization initiators when the substrate surface is exposed to a monomer. For a silicon wafer, optimal results are obtained when the surface water coverage is approximately a single monolayer, substantially homogenously across the substrate surface. Surface water film thickness significantly less than or greater than optimal coverage will result in sub-optimal formation of AP plasma-induced activation sites. Surface water coverage can be
10 achieved by placing the inorganic substrate in a controlled humidity environment, i.e., a humidity chamber with temperature and relative humidity (RH) control. Typical RH values are 20-70%, with optimum results achieved at ~ 50% RH at 22°C. Alternatively, water can be included with the plasma precursor and/or carrier gas(es) to promote surface peroxide formation.

15 [0046] Surface activation of an inorganic substrate using an AP plasma can be achieved even in the absence of an adsorbed water layer, though active site density will be significantly lower than when a layer of adsorbed water is present.

[0047] After cleaning and conditioning the silicon wafer, the wafer is exposed to an AP plasma either in an enclosed container under an inert gas (e.g., nitrogen, argon, etc.) or in an open environment of ambient air. Figure 2 schematically illustrates one nonlimiting example 20 of an AP plasma apparatus suitable for use in the practice of the invention. As shown, the apparatus can include or be housed in a glove bag or other chamber in which a substrate can be placed, and includes a plasma source, a radio frequency (RF) power generator, a controller (e.g., a microprocessor) coupled to the RF power generator and a matching network, a laminar flow mixer and mass flow controllers for introducing a plasma precursor gas/carrier 25 gas into the system, an inlet for nitrogen gas, and an outlet line that may be coupled to a gas pump. The plasma source produces a plasma stream that emanates from an outlet having a preferred geometry (e.g., rectangular or circular) and impinges upon the substrate surface. The outlet line and nitrogen inlet permit the chamber to be purged and flushed with nitrogen 30 prior to use. However, the chamber is maintained under atmospheric pressure during the surface activation and graft polymerization process.

[0048] In another embodiment (not shown), the glove bag or other chamber is omitted, and an AP plasma is simply generated and directed at a substrate surface in an open environment. In that case, the nitrogen inlet, vacuum line, and vacuum pump are not needed.

35 [0049] Additional, nonlimiting details about AP plasma generators are found in Schutze, A.; Jeong, J. Y.; Babayan, S.E.; Park, J. Selwyn, G.S.; Hicks, R.F. *IEEE Trans. Plasma Sci.* 1998, 26, (6), 1685-1694, which is incorporated by reference herein.

1 plasma gas, RF power, electrode voltage, treatment time, gas flow rate, gas partial pressure, total pressure, and gas temperature. Plasma treatment can be achieved by using one or more plasma precursor gases; nonlimiting examples include hydrogen, oxygen, nitrogen, air, carbon dioxide, water, fluorine, helium, argon, neon, ammonia, and methane, optionally in
5 combination with a carrier gas, for example, helium.

[0051] Hydrogen plasma, which is commonly used in nanoelectronics for surface cleaning, is composed of hydrogen atoms formed by electron impact dissociation, which may either recombine further downstream of the discharge region or can be used for surface treatment. Hydrogen plasma has an intrinsically low silicon etch rate, and can be operated at
10 low processing temperatures, unlike oxygen plasma which requires a high power density for processing. For example, in some embodiments, the hydrogen plasma gas temperature did not exceed 100°C over an exposure period of 60 s at RF power of 60 W.

[0052] Activating the substrate surface with an AP plasma provides a number of advantages over surface activation using a low pressure plasma, particularly where the AP
15 plasma is generated using a plasma jet. The advantages pertain both to the configuration and operating parameters of the AP plasma generator and to the properties of the generated plasma gas, and are especially evident when one compares plasma jet AP plasma activation to dielectric barrier discharge (DBD) plasma activation.

[0053] A DBD plasma source is typically designed in a parallel plate configuration, in
20 which two parallel plates are separated from one another by at most a few millimeters. Plasma particles exit the top electrode in small, independent microarcs and travel to the bottom electrode. The microarcs are about 100 µm in diameter and may be separated by as much as 2 cm. Because of the configuration and spacing of the streamers, this method results in a non-uniform plasma discharge. In addition, the breakdown voltage, which is the minimal
25 voltage needed to sustain plasma generation, is 5-25 kV. In terms of scale-up potential, the parallel plates are fixed and the electrode spacing cannot be increased. Also, the DBD source cannot be moved to scan the surface during plasma surface treatment.

[0054] In contrast, an AP plasma jet is a source consisting of two concentric electrodes from which plasma is discharged. The source can be easily positioned over a substrate for
30 surface treatment. The plasma discharge is spatially and temporally uniform and may be operated at various flow rates. The breakdown voltage for the plasma jet is in the range of 0.05-0.2 kV, significantly lower than for DBD sources. Also, the plasma jet operates over a wider and more stable voltage range than for the DBD source. The plasma jet maintains low processing gas temperatures for certain plasmas, which is ideal for graft polymerization onto thermally sensitive materials. The plasma jet offers many advantages for scale-up potential,
35 as a fixed source that can be positioned at different lateral spacing arrangements or as a moveable source.

1 [0055] The properties of the generated plasma gas are also different for the two
techniques. The DBD source operates over an electron temperature range of 1-10 eV, which
results in a plasma gas temperature that approaches 200°C. The electrons and ions exist for
only a short period of time (less than about 100 ns), which limits the effectiveness of surface
5 treatment. The density of plasma species, for example oxygen in helium, is about 10^{12} particles/cm³. The density of charged species, on the other hand, is approximately 10^{12} - 10^{15} particles/cm³.

[0056] In contrast, the hydrogen plasma jet operates over a lower electron
temperature range of 1-2 eV, which corresponds to a gas temperature of under 100°C
10 (slightly higher for oxygen plasma). For oxygen plasma, the activated oxygen atoms exist in
the excited state for up to 80 mm from the gas exit region. The density of plasma species, for
example oxygen in helium, is about 10^{16} particles/cm³, four orders of magnitude higher than
for DBD sources. The density of charged species, on the other hand, is approximately 10^{11} -
15 10^{12} particles/cm³. This significantly higher plasma species density enables substrate
surfaces to be modified to a much greater extent, allowing very dense active site formation.
Subsequent contact with a polymerizable monomer results in the formation of a very dense
array of grafted polymer chains bound to the surface, with average polymer separations at
least as small as 10nm.

[0057] Exposing the conditioned substrate to an atmospheric pressure plasma results in
20 the formation of a dense, substantially homogeneous array of surface-bound active sites
("polymer initiation sites") on the substrate surface, i.e., functional groups capable of
initiating polymerization upon exposure to a monomer. Nonlimiting examples of such
groups include peroxides, oxides, hydroxyls, amines, hydrides, epoxides, and radicals. For
dilute hydrogen in helium (1:99 H₂:He), a dense array of active surface sites for graft
25 polymerization can be achieved by varying RF power from about 20 to 60 W, with plasma
treatment times ranging from about 5 to 120 seconds. For a silicon substrate and a hydrogen-
helium plasma, the highest surface coverage of active sites were obtained at an RF power of
about 40 W and a plasma treatment time of about 10 s (the same was true for AP plasma-
treatment of a polymeric substrate). Optimal conditions (highest density of surface active
30 sites for polymerization initiation) may vary, however, depending on the nature of the
substrate surface, the plasma gas, and the desired level of surface activation. The amount of
adsorbed surface water, as well as the plasma power, treatment time, and other processing
parameters are variable and can be controlled as necessary to maximize active site --and,
ultimately, graft polymer-- density.

35 [0058] Surface functionality can also be adjusted by exposing the plasma-treated surface
to a desired gas or liquid immediately following plasma treatment. For example, exposing a
plasma-treated surface to air, pure oxygen, or water can lead to the formation of peroxide
groups. In one experiment, extending the period of exposure to water or oxygen for up to 2

1 minutes did not significantly reduce the concentration of surface active groups. Surface activation can be achieved also without immersing the plasma-modified surface in a gas or liquid. In addition, water can be included with the plasma precursor and/or carrier gas(es) to promote formation of surface peroxides.

5 [0059] After activating the substrate surface with AP plasma for a desired time, an ethylenically unsaturated monomer or monomer solution is introduced and allowed to contact the polymer initiation sites on the surface of the substrate, thereby facilitating polymer chain growth directly from the surface of the substrate. The polymer chains are covalently bound to the substrate through the active site moieties or their residues.

10 [0060] Any ethylenically unsaturated monomer that can be polymerized in a liquid phase reaction mixture via classical free radical polymerization or controlled radical polymerization can be used. Nonlimiting examples include vinyl and divinyl monomers, with specific examples being methacrylic acid, acrylic acid, other acid vinyl monomers, acrylic and methacrylic esters, such as methyl methacrylate and butyl acrylate, polar vinyl monomers such as vinyl pyrrolidone and vinyl pyridine, and non-polar vinyl monomers, such as styrene and vinyl acetate. 1-Vinyl-2-pyrrolidone (VP) is of interest because poly(vinyl pyrrolidone) has excellent biocompatible properties, has been proposed as a surface modifier to reduce membrane fouling, and is miscible in both aqueous and organic media. Combinations of two or more monomers can be used to form graft copolymers.

15 [0061] The ethylenically unsaturated monomers can be provided as pure monomer in the liquid phase or as a monomer solution, and is allowed to contact the plasma-treated surface for a time and at a temperature sufficient to cause graft polymer chains to grow from the surface of the substrate.

20 [0062] Notably, the choice of solvent can play an important role in facilitating graft polymerization from the surface of the substrate, as it allows for increased miscibility (i.e., solubility) between the monomer(s) and the surface of the substrate, and, therefore, improved monomer wetting power. For example, for hydrophilic (i.e., polar) monomers, water and/or another polar solvent can be used. Nonlimiting examples include N-methyl-2-pyrrolidone, tetrahydrofuran, and alcohols. For hydrophobic (i.e., non-polar) monomers, the solvent will typically be non-polar, for example, chlorobenzene or toluene. Mixtures of solvents can be used. As a general rule of thumb, the highest surface densities of grafted polymer chains are obtained with monomer-solvent pairs having high surface wetting power with plasma surface initiation achieved at the optimal conditions.

25 [0063] Polymer growth from the plasma-activated substrate surface may be directed either by classical free-radical graft polymerization or by controlled "living" graft polymerization. In the former, polymerization is controlled by initial monomer concentration, reaction temperature, reaction time, and optionally the use of chain transfer agents, and results in surfaces with highly polydisperse polymer chain length (typically $pI \geq$

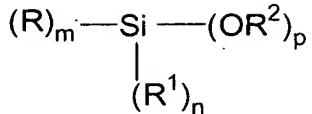
1 2). With controlled "living" graft polymerization, surfaces having a high density of grafted
polymer chains with a uniform chain size distribution ($pI < 1.5$) can be achieved. In theory,
polymerization can proceed to completion, i.e., until the monomer is exhausted.

5 [0064] Nonlimiting examples of suitable controlled "living" polymerization approaches
include those that require a free-radical molecule (i.e., a free radical control agent) in solution
to control polymerization, such as Reversible Addition Fragmentation Transfer (RAFT)
Polymerization and Nitroxide-Mediated Graft Polymerization (NMGP). For NMGP, a
stoichiometric amount of free-radical molecules is added to the reaction mixture with a
10 plasma-activated surface and controls growth of the free-radical polymer propagating from
the surface. Nitroxide-mediated polymerization using a 2,2,6,6-tetramethyl-1-piperidinyloxy
(TEMPO) control agent is described below in Example 5.

15 [0065] After graft polymerization, the modified surface can be washed in an appropriate
solvent to remove physically adsorbed homopolymer (or copolymer, if two or more
monomers were used in the polymerization). Thus, water or another polar solvent is used to
remove adsorbed polar homopolymers (e.g., poly(vinyl pyrrolidone), and a non-polar solvent,
for example, toluene, is used to remove adsorbed non-polar homopolymers (e.g.,
polystyrene).

20 [0066] In another embodiment of the invention, APPIG polymerization is used to modify
the surface of an inorganic substrate other than silicon, for example, any of the previously
25 listed metals, metalloids, metal oxides, and other metallic or ceramic materials capable of
supporting the formation of surface active sites. As with the silicon wafer, the method
comprises the steps of surface cleaning and conditioning, formation of active sites on the
surface using an AP plasma, and contacting the active sites with a monomer or monomer
solution to facilitate the formation and growth of graft polymer chains from the substrate
surface.

30 [0067] In another embodiment of the invention, an organo-functionalized inorganic
substrate is modified by APPIG polymerization. For example, silica and similar materials
can be vinyl-functionalized (i.e., silylated with a vinyl group-containing silyl molecule) by
35 (a) hydrolysis and (b) reaction with a vinyl-substituted molecule, yielding vinyl-
functionalized surfaces that can be activated by AP plasma treatment and then allowed to
contact a monomer or monomer solution, which causes end-grafted polymer chains to grow
from the surface of the substrate. The use of vinyl lower alkoxy silanes to activate inorganic
oxide surfaces is described in U.S. patent no. 6,440309 (Cohen), the entire contents of which
are incorporated by reference herein. Briefly, the method entails the formation of surface
hydroxyl groups (using, e.g., an aqueous acid solution), followed by reaction with a vinyl
activation (e.g., a vinyl-silane). Representative vinyl activators include vinyl alkoxy silanes,
having the following formula:



1 wherein R is an organic group; R¹ is an organic group containing at least one vinyl functional group; R² is a lower alkyl (i.e., C1-C3 alkyl); m is 0, -1 or 2; n is 1 to 3; p is 1 to 3; and the sum of m, n, and p is 4. Specific, nonlimiting examples of vinyl lower alkoxy silanes include diallyl dimethoxy silane, allyl triethoxy silane, ethyl vinyl dimethoxy silane, divinyl diethoxy silane, vinyl triethoxy silane, and vinyl trimethoxy silane. In one embodiment of the invention, atmospheric pressure plasma is used to oxidize the vinyl group, creating peroxides that act as polymerization initiators for subsequent graft polymerization of monomers. Plasma may also be used to oxidize and create peroxides from other unsaturated groups, such as azides, carbonyls, etc. However, it is not necessary for the surface activation sites to be unsaturated groups, and any organic or inorganic group may be treated with plasma to create surface initiation sites for polymerization, including but not limited to surface radicals and peroxides.

5 [0068] In another significant embodiment of the invention, the surface of a polymeric substrate is modified by graft polymerization using an AP plasma. In principle, any organic or inorganic polymer can be treated according to the method of the present invention.

10 Nonlimiting examples of inorganic polymers include polystyrene, polyamides, and polysulfones. The polymeric substrate is exposed to an AP plasma, which causes surface-bound active sites (polymer-initiation sites) to form on the substrate. Contacting the active sites with a monomer solution facilitates the formation and growth of polymer chains, which are covalently bound to the substrate through an active site moiety or moiety residue.

15 [0069] Surface modification of a polymeric substrate can utilize any of the plasma precursor gases listed above, optionally with a carrier gas. Typically, the surface of the polymeric substrate to be modified will be clean (i.e., substantially free of contaminants), but aggressive acids, such as piranha solution, will not generally be employed for this purpose. Instead, the substrate is simply immersed in or rinsed with one or more solvents, and then dried prior to AP plasma treatment. Conditioning in a humidity chamber is typically unnecessary, as active site formation results from the interaction between energetic plasma species and chemical moieties intrinsic to the polymeric substrate itself. However, water can be introduced into the plasma precursor and/or carrier gas stream(s) so as to provide for additional control of the formation of surface active sites, such as peroxides. The amount of adsorbed surface water, as well as the plasma power, treatment time, and other processing parameters are variable and can be controlled as necessary to maximize active site --and, ultimately, graft polymer-- density.

1 [0070] Graft polymerization from a polymeric substrate can be carried out using a liquid
monomer or monomer solution, with any desired unsaturated monomer. For example, graft
polymerization of 1-vinyl-2-pyrrolidone (a polar vinyl monomer) was achieved, after AP
plasma activation (using a hydrogen plasma), in an aqueous reaction mixture (20% v/v
5 monomer concentration at 80°C), and resulted in a thin, dense polymer film having a
thickness of about 80 angstrom after 2 h. Similarly, graft polymerization of methacrylic acid
(an ionic vinyl monomer) was achieved, after AP plasma activation (using a hydrogen
plasma), in an aqueous methacrylic acid solution (20% v/v monomer concentration at 60°C),
and resulted in a thin, dense polymer film having a thickness of about 40 angstrom at after 2
10 h.

[0071] Modifying polymeric surfaces by atmospheric pressure plasma-induced graft
polymerization according to the invention allows one to impart greater surface adhesion to
polymeric materials; to control surface wetting, water resistance, and solvent resistance for
plastic materials; to engineer surface chemical functionality, chemical selectivity, and surface
15 topology for chemical sensors; to increase wear resistance; to improve biocompatibility for
medical devices; and to decrease surface fouling (e.g., organic fouling, biofouling, and
mineral salt scaling) for separation membrane applications.

Examples

20 [0072] Using the materials and methods described below, several nano-structured silicon,
organic-functionalized, and polymeric substrates were prepared in accordance with the
invention (Table 1).

Table 1 - Examples

<u>Ex.</u>	<u>Substrate</u>	<u>Monomer</u>	<u>Solvent</u>	<u>Polymerization Technique</u>
1	silicon	1-vinyl-2-pyrrolidone	DI water	FRGP
2	silicon	1-vinyl-2-pyrrolidone	1-methyl-2-pyrrolidone	FRGP
3	silicon	1-vinyl-2-pyrrolidone	DI water/1-methyl-2-pyrrolidone	FRGP
4	silicon/vinyl trimethoxysilane	1-vinyl-2-pyrrolidone	DI water	FRGP
5	silicon/vinyl trimethoxysilane	1-vinyl-2-pyrrolidone	1-methyl-2-pyrrolidone	FRGP
6	polysulfone	1-vinyl-2-pyrrolidone	DI water	FGRP
7	silicon	styrene	chlorobenzene	FRGP

1	8	silicon	styrene	chlorobenzene	NMGP
9	silicon	styrene	toluene	FRGP	
10	10	silicon	vinyl acetate	ethyl acetate	FRGP
5	11	silicon/vinyl trimethoxysilane	vinyl acetate	ethyl acetate	FRGP
12	12	silicon/vinyl trimethoxysilane	4-vinyl pyridine	methoxy propanol	FRGP
13	13	aromatic polyamide	methacrylic acid	DI water	FRGP
14	14	aromatic polyamide	acrylic acid	DI water	FRGP

10

[0073] Materials. Prime-grade silicon <100> wafers were obtained from WaferNet, Inc. (San Jose, CA). Native wafer samples were single-side polished and cut into 1x1 or 2x2cm square pieces for processing. De-ionized (DI) water was produced using a Millipore (Bedford, MA) Milli-Q filtration system. Hydrofluoric acid, sulfuric acid, aqueous hydrogen peroxide (30%), technical grade hydrochloric acid, chlorobenzene (99%), and tetrahydrofuran were purchased from Fisher Scientific (Tustin, CA). Anhydrous n-methyl-2-pyrrolidone (99.5%), reagent grade toluene, and tetrahydrofuran were obtained from Fisher Scientific (Tustin, CA). 1-Vinyl-2-pyrrolidone (99%) with sodium hydroxide inhibitor (<0.1%) was used as received and was obtained from Alfa Aesar (Ward Hill, MA). Styrene (99%) with catechol inhibitor (<0.1%), obtained from Sigma Slrdich (St. Louis, MO), was purified by column chromatography using a silica column (Fisher Scientific, Tustin, CA). Aqueous ammonium hydroxide (50%) was purchased from LabChem, Inc. (Pittsburg, PA). 2,2,6,6-Tetramethyl-1-piperidinyloxy radical (TEMPO, 98%), obtained from Sigma Aldrich (St. Louis, MO), was used for surface radical determination and as a control agent for nitroxide-mediated graft polymerization.

[0074] Silicon Surface Preparation. Silicon substrates were subjected to a multi-step surface cleaning and conditioning process to remove surface contaminants and the native oxide layer on as-received wafers. Substrates were cleaned in piranha solution (7:3 (v/v) sulfuric acid/hydrogen peroxide) (Ex. 1-3, 7-10) for 10 minutes at 90°C and then triple rinsed to remove residuals. Substrates were then dipped in a 20% (v/v) aqueous solution of hydrofluoric acid to remove the native oxide layer, and then triple rinsed as before. For hydrophilic (i.e., polar) vinyl monomer graft polymerization (Ex. 1-3), the silicon substrates were immersed in 1% (v/v) aqueous hydrochloric acid at ambient temperature for 8 h and then placed in DI water for 1 h to fully hydroxylate the silicon surface (i.e., to create surface hydroxyls, which increase the hydrophilicity of the wafer surface). Hydrolyzed silicon wafers were then oven dried under vacuum at 100°C for 10 h to remove surface water. For hydrophobic (i.e., non-polar) polymerization (Ex. 7-10), surface hydrolysis was not required.

1 [0075] Silylated Silicon Surface Preparation. Silicon substrates were silylated (Ex. 4-5, 11-12) by first cleaning in piranha solution (7:3 (v/v) sulfuric acid/hydrogen peroxide) for 10 minutes at 90°C and then triple rinsed to remove residuals. Substrates were then dipped in a 20% (v/v) aqueous solution of hydrofluoric acid to remove the native oxide layer, and then
5 triple rinsed as before. The silicon substrates were immersed in 1% (v/v) aqueous hydrochloric acid at ambient temperature for 8 h and then placed in DI water for 1 h to fully hydroxylate the silicon surface (i.e., to create surface hydroxyls, which increase the hydrophilicity of the wafer surface). Hydrolyzed silicon wafers were then oven dried under vacuum at 100°C for 10 h to remove surface water. Hydrolyzed silicon surfaces were
10 silylated (Ex. 4-5, 11-12) by immersion in a 10% (v/v) mixture of vinyl trimethoxysilane in toluene and allowed to react for the desired period (typically not longer than 24 hours) at ambient temperature. Silylated silicon substrates were sonicated in toluene, washed in tetrahydrofuran, and dried overnight in a vacuum oven.

15 [0076] Polymer Surface Preparation. Polymeric substrates (Ex. 6, 13, 14) were generally cleaned by a stream of nitrogen gas to remove surface adsorbed particles.

[0077] Graft Polymerization of Silicon. Graft polymerization from the AP plasma-treated surfaces on silicon was achieved by immersing the substrates in a monomer solution. For graft polymerization of 1-vinyl-2-pyrrolidone (Ex. 1-3), initial monomer concentrations of 10-50% (v/v) were used for graft polymerization in water solvent (Ex. 1), and n-methyl-2-pyrrolidone solvent (Ex. 2). Also, graft polymerization of 1-vinyl-2-pyrrolidone was demonstrated on silicon for an initial monomer concentration of 30% (v/v) in a mixture of water and n-methyl-2-pyrrolidone (Ex. 3). The pH for aqueous polymerization reaction mixtures was adjusted with ammonium hydroxide to reduce side reactions. The temperature of the reaction mixture was maintained at 80°C ($\pm 1^\circ\text{C}$) and each reaction was allowed to proceed for a period of at least 8 h. Following the reaction, the surface modified silicon substrates were triple-rinsed in DI water and then sonicated to remove potentially adsorbed homopolymer. Cleaned substrates were then oven dried overnight under vacuum at 100°C.
20 In Ex. 2, surface chain coverage, observed by Atomic Force Microscopy, demonstrated a thin dense polymer film with a film thickness of about 55 angstrom, polymer chain spacing in the range of 5-10 nm, and an average feature diameter of about 17 nm. Other results are
25 presented below.

[0078] In Ex. 7 and 9, the hydrogen plasma-treated silicon substrates were grafted in a mixture of styrene in chlorobenzene (Ex. 7) and toluene (Ex. 9) solution, with an initial monomer concentration range of 10-50% (v/v) at T = 70°C, 85°C, and 100°C. Following the reaction, the surface modified silicon substrates were sonicated in toluene, cleaned in tetrahydrofuran, and dried in a vacuum oven. Polymer film thickness, measured by ellipsometry, demonstrated steady polymer film thickness for surface modification at an initial monomer concentration of 30% (v/v) in chlorobenzene at 70 and 85°C. The polymer
30

1 film thickness for the grafted film at 30% (v/v) styrene at 85°C after 20 h was 120 angstrom. The rate of polystyrene film growth was dependent on the reaction temperature and initial monomer concentration, but graft polymerization at 30 and 50% (v/v) styrene at 100°C resulted in poor control over film growth and heterogeneous surface topology.

5 [0079] In Ex. 8, the substrates were grafted in a 50% mixture of styrene in chlorobenzene solution at a temperature range of 100-130°C (120°C) and TEMPO control agent concentration of 5-15mM, at a reaction time of 72 h. Following the reaction, the polymer-modified silicon substrates were sonicated to remove surface adsorbed homopolymer, rinsed in tetrahydrofuran, and dried at 100°C. In Ex. 8, controlled and improved 10 surface chain growth was accomplished by plasma-initiated nitroxide mediated graft polymerization with styrene in chlorobenzene with TEMPO control agent at [T]=5 - 15 mM at a reaction temperature of 120°C, initial monomer concentration of 50% v/v and a reaction period of 72 h. The polymer film growth for controlled nitroxide mediated graft polymerization increased linearly with time at [T]=10 mM, reaching a film thickness of about 280 angstrom. In addition, the surface roughness was 0.52 nm, which is similar to the 15 surface roughness expected for smooth native silicon wafers. Linear polymer film growth with time and a low surface roughness indicates that the plasma-induced nitroxide graft polymerization is a controlled free-radical polymerization reaction.

[0080] In Ex. 10, the hydrogen plasma-treated silicon substrates were grafted in a mixture 20 of vinyl acetate in ethyl acetate, with an initial monomer concentration range of 10-30% (v/v) at T = 50°C, 60°C, and 70°C.

[0081] Graft Polymerization of Silylated Silicon. Silylated silicon substrates (Ex. 4,5,11,12) were graft polymerized by plasma surface treatment and immersion in a monomer 25 solution. Graft polymerization of 1-vinyl-2-pyrrolidone was achieved over a monomer concentration range of 10-50% (v/v) at 80°C for a period of 8 h in both a DI water solvent (Ex. 4) and n-methyl-2-pyrrolidone (Ex. 5). Following the reaction, the modified surface was cleaned in DI water then sonicated to remove potentially adsorbed homopolymer. Cleaned substrates were then oven dried overnight under vacuum at 100°C. Silylated silicon was also modified by vinyl acetate (Ex. 11) and vinyl pyridine (Ex. 12). Vinyl acetate graft 30 polymerization was conducted at 30% (v/v) monomer concentration in ethyl acetate at 60°C for a period of 8 h. Vinyl pyridine graft polymerization was conducted at 30% (v/v) monomer concentration in methoxy propanol at 80°C for a period of 8 h.

[0082] Graft Polymerization of Polymer Surfaces. Polysulfone (Ex. 6)was modified by 35 plasma-induced graft polymerization of 1-vinyl-2-pyrrolidone in DI water. The initial monomer concentration was 20% (v/v) at 70°C for a period of 2 h. Polyamide was also modified by plasma-induced graft polymerization of methacrylic acid (Ex. 13) and acrylic acid (Ex. 14) in DI water. The initial monomer concentration was in the range of 5-20% (v/v) over a temperature range of 50-70°C for a period of 2 h for both monomers. The film

1 thickness that was achieved for grafting polymethacrylic acid from polyamide surfaces was
about 40 angstrom at 20% (v/v) monomer concentration for 2 h at 60°C.

5 [0083] Surface Initiator Determination. The presence and relative abundance of surface
radicals that are formed during plasma treatment were determined using 2,2,6,6-tetramethyl-
1-piperidinyloxy (TEMPO), a well known free-radical scavenger that covalently bonds to
silicon surface radicals. The presence of surface-bound TEMPO (as detected by FTIR)
served as an indirect measure of the density of surface radicals. For example, silicon
substrates (1x1 cm) were plasma treated and immediately immersed in a solution of 0.1 mM
TEMPO dissolved in n-methyl-2-pyrrolidone and allowed to react over a 24 h period at 90°C.
10 The substrates were then removed and sonicated in tetrahydrofuran for two hours to remove
surface adsorbed TEMPO and finally oven dried under vacuum at 100°C for a sufficient
period of time to remove residual solvent.

15 [0084] Grazing Angle FTIR spectroscopy was used to detect the surface-bound TEMPO
by collecting spectra from at least 3 locations for each wafer. The presence of TEMPO was
confirmed by FTIR absorption peaks at 3019 cm^{-1} and 1100 cm^{-1} for aromatic carbon atoms
and nitroxide functional groups, respectively. The absorbance spectrum was compared with
the solution concentration to develop the linear calibration curve between concentration and
absorbance over the initial TEMPO concentration range of 1.0-0.001 mM.

20 [0085] Surface Characterization. Surface analysis by Fourier Transform Infrared (FTIR)
Spectroscopy was carried out using a Bio-Rad FTS-40 with a grazing angle attachment
(Varian Digilab Division, Cambridge, MA) (Ex. 1-3) or Attenuated Total Reflectance Fourier
Transform Infrared (ATR-FTIR) spectroscopy using a BioRad FTS-40 FTR equipped with an
Attenuated Total Reflectance accessory (BioRad Digilab Division) (Ex. 4 and 5). Grazing
angle IR spectra for TEMPO-reacted surfaces and plasma-treated surfaces were processed by
25 subtraction from the spectra for clean, native substrates. Resulting spectra were represented
in Kubelka-Munk units which have absorbance values that are proportional to the surface
species concentration.

30 [0086] Contact angle measurements for the poly(vinyl pyrrolidone) grafted substrate
surfaces were obtained by the sessile-drop method with a Kruss Model G-23 contact angle
instrument (Hamburg, Germany). Before the measurements, each polymer-grafted substrate
was rinsed and sonicated separately in tetrahydrofuran and then DI water, each for 15 min.
The polymer-grafted substrate was subsequently oven-dried under vacuum at a suitable
temperature to promote drying but avoid thermal damage to the substrate and the grafted
polymer layer. For example, 30 min drying time at 80°C was adequate for the poly(vinyl
35 pyrrolidone) grafted silicon wafer. Contact angle measurements were made using DI water at
40-50% relative humidity and 22°C. Each contact angle datum was obtained by averaging
the results from 5 separate drops on different areas of a given surface. The size and volume

1 of the drops were kept approximately constant to reduce variations in contact angle
measurements.

5 [0087] The film thickness of the plasma treated surface and the polymer grafted substrates was determined using a Sopra GES5 Spectroscopic Ellipsometer (SE) (Westford, MA). The broadband variable angle SE was operated over a range of 250-850 nm and the ellipsometric data collected were fitted to user defined multi-layer film models with the film thickness calculated through the use of the Levenberg-Marquardt regression method. Each measurement was averaged over five locations on the substrate and the standard deviation did not exceed 10%.

10 [0088] Atomic Force Microscopy (AFM) imaging was performed using a Multimode AFM with a Nanoscope IIIa SPM controller (Digital Instruments, Santa Barbara). All AFM scans were taken in tapping mode in ambient air using NSC15 silicon nitride probes (Digital Instruments, Veeco Metrology Group, Santa Barbara, CA) with a force constant between 20-70 N/m, a nominal radius of curvature of 5-10 nm and a side angle of 20°. AFM scans (1x1 μm) on silicon substrates were taken at a scan rate of 0.5-1 Hz. At least five locations were sampled for each modified substrate, with two scans taken for each location. Surfaces were imaged at 0 and 90° to ensure that images were free of directional errors. Height data and phase data were taken simultaneously for the same scan area. Root-mean-square (RMS) surface roughness was determined directly from height data for 1x1 μm scans where R_{rms} is the RMS roughness, Z_i is the i th height sample out of N total samples, and Z_{avg} is the mean height.

$$R_{rms} = \sqrt{\frac{\sum(Z_i - Z_{avg})^2}{N}} \quad (1)$$

25 The skewness, S_{skew} , which is a measure of the asymmetry of the height distribution data about the mean, was determined from

$$S_{skew} = \frac{\sum(Z_i - Z_{avg})^3}{(N - 1)\sigma^3} \quad (2)$$

30 where σ is the standard deviation. Polymer volume for the graft polymerized surfaces was determined over a 1x1 μm area by volume integration over the grafted polymer area with respect to the z-height profile of the polymer surface features. To minimize the contribution of native surface features to the grafted polymer volume, the average Z-height of the native substrate surface, determined from five locations for each surface, was subtracted from the surface feature height data when integrating to obtain the total grafted polymer volume. For determining the height distributions of the modified surfaces, the Z-height data used for 35 polymer volume measurements was compared to a Gaussian distribution in order to clarify the presence of tails (small or large features) in the distribution. Feature spacing and average

1 feature diameter were determined by measurements taken from ten different locations over a 1x1 μm area, whereby feature boundaries were defined based on digital image pixel analysis.

5 [0089] Consistent with previous studies on plasma activation of polymeric substrates, the resulting surface density of surface initiation sites was, in part, determined by the plasma treatment time and the radio frequency (RF) power. However, it was found that, for inorganic substrates, formation of a high density of active sites (and, hence, a dense graft polymer layer) required careful control of the amount of water adsorbed on the surface of the substrate. Adsorbed surface water was not required with polymeric substrates. The combined effect of plasma surface treatment and adsorbed surface water on the generation of 10 surface initiation sites was evaluated using a TEMPO binding assay.

[0090] The presence of surface radical species generated by AP hydrogen plasma surface treatment of the substrates was verified using the TEMPO binding assay. The impact of both plasma treatment time and RF power were first evaluated to select the optimal plasma treatment conditions. The surface density of radical species, as suggested by the TEMPO 15 surface binding analysis, increased with plasma exposure times according to a power law dependence as illustrated in FIG. 3 up to a maximum coverage that was reached at 10 s treatment time (RF power of 40 W). For the silicon substrate, extending the plasma treatment time beyond 10 s resulted in a similar decline in radical surface coverage by more than 70% and 90% at 20 and 30 s exposure periods, respectively. These findings are in general 20 agreement with other studies performed on organic materials in which an optimal plasma exposure treatment time was found which maximized surface radical density. This behavior is due to surface radical formation and subsequent passivation, leading to removal or inactivation of surface initiators as the residence time of hydrogen plasma species is increased at the surface. However, it should be noted that the treatment time interval 25 necessary for optimal surface radical formation using low pressure plasma activation of polymeric materials was reported to be significantly longer than for AP plasma treatment of inorganic surfaces: 180 s for argon plasma treatment of polyethylene, 60 s for argon plasma treatment of polyacrylic acid, and 30 s for oxygen plasma treatment of polyurethane.

[0091] RF plasma power had a qualitatively similar effect as treatment time on the 30 formation and surface coverage of radical initiator sites as shown in FIG. 4. The site density of surface radicals increased with RF plasma power to a maximum reached at RF power of 40 W (treatment time of 10 s) and then decreased slowly with a further increase in the RF power. In plasma processing, an increase in RF plasma power leads to increased electron-atom collisions in the gas phase, generating a higher density of reactive species in the plasma gas 35 and therefore at the substrate surface. Thus, similar to the impact of increased plasma treatment time, radicals that were created on the surface were subsequently passivated by overexposure to plasma species.

1 [0092] Consideration of the surface chemistry involved in stabilization of surface radicals
on inorganic substrates led to further strategies which improved surface radical number
density. While the chemical surface properties of polymeric surfaces allow for the formation
5 of pseudo-stable initiation sites (e.g., epoxides) upon plasma treatment, inorganic surface
radicals are unstable and undergo molecular rearrangements such as atomic recombination
and/or decomposition to form non-radical dormant species. To maintain surface activity (for
subsequent graft polymerization) for a sufficiently long period, it was found in the present
study that adsorbed surface water was critical in the formation and stabilization of inorganic
10 substrate surface radicals. Although not bound by theory, it is postulated that the beneficial
role of adsorbed surface water may be the result of the reaction of surface radicals with water
to form surface peroxides or possibly due to stabilization of the silicon radical through
hydrogen bonding with water. Accordingly, the impact of surface water on the creation of
surface initiation sites was evaluated in a series of experiments in which the degree of surface
water coverage was varied by equilibrating the substrate in a humidity controlled chamber.

15 [0093] As shown in FIG. 5, the density of surface radicals, as implied by the TEMPO
binding analysis, increased with increasing adsorbed surface water coverage up to a
maximum at 50% relative humidity (% RH) at 22°C (for the optimal plasma exposure of 10 s
at RF power of 40 W). As previously noted elsewhere, for fully hydroxylated silica surfaces
with a silanol concentration of 7.6 $\mu\text{moles}/\text{m}^2$, the formation of a single adsorbed monolayer
20 of water occurs at about 51% RH at 22°C, assuming a 1:1 surface water to silanol ratio.
Thus, it may be inferred that the maximum density of surface active sites obtained in the
present study at 50% RH corresponded to approximately a single monolayer coverage of
surface water. At surface water coverage above a monolayer, a significant decrease of 90%
in surface radical density occurred as the relative humidity increased from 50% to 60%. It is
25 noted that the atomic radius of a hydrogen plasma species is approximately 0.5 Å while the
film thicknesses of adsorbed surface water for 1, 2 and 3 monolayers are 1.2, 2.7, and 4.3 Å,
respectively. It is believed that as the surface water layer thickness increased, the water film
became a physical barrier to plasma particles, thereby reducing direct interactions with the
underlying surface. The above results illustrate that optimal control of surface water
30 coverage on inorganic substrates, along with plasma treatment time and RF power, was
essential for control of the density of surface initiation sites necessary for graft
polymerization.

[0094] AFM imaging of the silicon wafers demonstrated that the RMS surface roughness
of the native silicon wafer ($R_{rms}=0.17 \text{ nm}$) was essentially unaltered following surface
35 hydrolysis and AP plasma treatment ($R_{rms}=0.20 \text{ nm}$) over a treatment period of 60 s.
However, plasma treatment of the silicon substrate did result in an increased surface
hydrophilicity as indicated by the decrease in water contact angle with increased plasma
exposure period. It is noted, though, that at the optimal plasma activation exposure time for

1 surface radical formation (treatment time=10 s), the contact angle of the plasma treated
 surface decreased by only 13% relative to that of the untreated surface (i.e., from 61° to 53°).

5 [0095] APPIG polymerization of 1-vinyl-2-pyrrolidone (VP) onto a silicon substrate
 (silicon-g-PVP) was initially conducted at the optimal surface plasma activation conditions
 (10 s plasma exposure period, RF power of 40 W, and 50% RH at 22°C). The polymer
 modified surfaces were characterized by Atomic Force Microscopy with respect to surface
 feature number density and spacing, surface feature height distribution, RMS surface
 roughness (R_{rms} , eq 1) and polymer volume. Also, it was noted that the contributions of small
 features to surface roughness may be eclipsed by a lower density of larger surface features.

10 Therefore, the distribution of polymer surface feature heights and skewness (S_{skew} , eq 2) were
 analyzed to provide a more descriptive characterization of surface topography.

[0096] APPIG polymerization on a plasma-treated silicon substrate was initially
 performed in an aqueous solvent (e.g., Ex. 1), which is the most commonly used media for
 polymerization of VP. Results of graft polymerization in an aqueous solvent (Table 2),
 15 where the initial monomer concentration was increased from $[M]_0=10\%-50\%$ (v/v), revealed
 grafted polymer volume that was maximized at about $[M]_0=30\%$, with nearly a factor of nine
 increase in the polymer volume and an increase in surface roughness relative to $[M]_0=10\%$.
 Further, the RMS surface roughness ($R_{rms}=0.41$ nm) of the surface grafted at $[M]_0=30\%$ was
 20 about a factor of 2.4 greater than the RMS roughness of the native silicon wafer. As the
 initial monomer concentration was increased above 30%, the polymer volume decreased by
 more than 50% at $[M]_0=50\%$.

Table 2

Reaction Condition				
	[M] ₀ (v/v) ^(a)	T (°C)	R _{rms} (nm)	Polymer Volume (nm ³ /μm ²) (10 ³)
	10	80	0.18	5.9
	20	80	0.32	25.0
	30	80	0.41	52.3
	40	80	0.47	37.9
	50	80	0.36	24.8

^(a) Graft polymerization conducted in aqueous solvent. Note: Initial monomer concentrations of 10%, 20%, 30%, 40%, and 50% (v/v) are denoted in the text as M10, M20, M30, M40, and M50, respectively.

35 [0097] Water contact angle measurements (not shown) of PVP-grafted surfaces in an
 aqueous solvent did not evidence a measurable change (<5%) in surface hydrophilicity due to
 the low surface coverage of grafted polymers. AFM imaging of the silicon-g-PVP wafers
 created in the above aqueous graft polymerization step was used to reveal the topography of
 the modified surfaces (FIG. 6). While these studies were useful in identifying the optimal

1 monomer concentration for grafting at $[M]_0=30\%$, AFM imaging suggested that the above
grafting approach was not capable of producing high density surface grafting, which may
have been due, in part, to the aqueous solvent. Water contact angle measurements of the
hydrolyzed surface (61°) suggested a low degree of hydrophilicity, indicating poor solvent-
5 substrate surface wetting, which may have been insufficient for graft polymerization in the
aqueous solvent. N-methyl-2-pyrrolidone (NMP), an organic solvent miscible in both
monomer and substrate, was found to be a substitute solvent for DI water for improved
grafting density. Contact angle measurements with NMP as the wetting agent demonstrated
that the surface was completely wetted ($<5^\circ$) by the organic solvent.

10 [0098] Graft polymerization in NMP indeed resulted in a higher density of surface
grafted features as observed by AFM imaging (FIG. 7), evidencing a higher density of
polymer chains as compared to graft polymerization in an aqueous solvent. PVP grafted
surfaces obtained by graft polymerization in NMP demonstrated an increase in polymer
volume with increasing initial monomer concentration (Table 3), up to a maximum obtained
15 at $[M]_0=30\%$, qualitatively consistent with studies performed in aqueous solvent. Surfaces
grafted at $[M]_0=30\%$ as compared to those grafted at $[M]_0=10\%$ demonstrated both a 3-fold
increase in polymer layer thickness and a corresponding decrease of 30% in water contact
angle. The increase in grafted layer thickness with increasing initial monomer concentration
is consistent with previous work on the kinetics of free radical graft polymerization of 1-
20 vinyl-2-pyrrolidone that conclusively demonstrated a rise in surface polymer graft yield with
initial monomer concentration. It was observed, however, that when the initial monomer
concentration was increased above 30% (i.e., 40% and 50% as given in Table 2), there was a
decrease in the grafted polymer volume by 60% and 75%, respectively. Although the
polymer layer thickness obtained at $[M]_0=40\%$ decreased by about 51%, relative to the
25 maximum thickness attained at $[M]_0=30\%$, there was no apparent decrease in surface graft
density of polymer features. The increase in layer thickness with initial monomer
concentration (at approximately $[M]_0 \leq 30\%$) is as expected given the higher rate of monomer
addition to growing chains (i.e., propagation). However, chain termination (due to both chain
transfer and chain-chain termination) also increases with monomer concentration. Therefore,
30 the film thickness should drop at high initial monomer concentrations as reported in Table 3.
In principle, and as verified by data up to the initial monomer concentration of 40%, chain
surface density appeared to be affected primarily by the creation of active surface sites by the
plasma treatment process. Unexpectedly, however, at sufficiently high monomer
concentration, as observed for $[M]_0=50\%$, apparent feature spacing was reduced relative to
35 $[M]_0=30\%$ and 40%. Comparison of surfaces grafted in NMP solvent as opposed to an
aqueous solvent demonstrated a striking difference in surface feature spacing. For example,
for initial monomer concentration $[M]_0=30\%$, grafting in NMP solvent resulted in surface
feature spacing of 5 to 10 nm as compared to a range of 100 to 200 nm when grafting in an

1 aqueous solvent. Moreover, relative to aqueous studies, graft polymerization in NMP
 resulted in more than a 160% increase in grafted polymer volume, a 75% increase in surface
 roughness and a significant increase in polymer graft density.

5 Table 3

Reaction Condition							
	[M] ₀ (v/v) ^(a)	Temperature (°C)	Contact Angle (°)	Surface Roughness, R _{rms} (nm)	PVP Layer Thickness (nm)	Polymer Volume (nm ³ /μm ²) (10 ³)	Polymer Feature Spacing (nm)
10	10	80	54	0.18	1.74	20.1	25-35
	20	80	43	0.42	2.27	49.9	5-20
	30	80	38	0.72	5.50	138.9	5-10
	40	80	49	0.38	2.70	85.3	5-10
15	50	80	51	0.26	2.32	35.4	20-30

^(a) Graft polymerization conducted in pure n-methyl-2-pyrrolidone

[0099] It was found that, by adjusting the ratio of organic to aqueous media in the solvent mixture the surface morphology and polymer graft density could be uniquely tuned. As shown in Table 4, the average polymer feature diameter increased by nearly a factor of 9 at [NMP]=60% relative to pure aqueous solvent, and the feature spacing size decreased to a range of 10 to 50 nm, suggesting the formation of large, close proximity features on the surface. However, as the NMP:water ratio was further increased to [NMP]=80%, the feature diameter decreased by more than 50% and the feature spacing further decreased to a range of 5 to 20 nm, indicating the formation of a higher surface number density of smaller grafted polymer chains.

20 Table 4

Reaction Condition				
	[NMP] (v/v)	[M] ₀ (v/v)	Avg. Polymer Feature Diameter (nm)	Polymer Feature Spacing (nm)
30	0	30	10.51	100-200
	20	30	27.44	30-80
35	40	30	50.16	25-60
	60	30	92.33	10-50
	80	30	43.24	5-20
	100	30	17.06	5-10

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[00100] AFM images illustrate that the grafted PVP layer formed at [NMP]=60% (FIG. 8c) was composed of large clusters of grafted polymers compared to smaller grafted polymer features that resulted from grafting at [NMP]=40% (FIG. 8b) as well as at [NMP]=15% (FIG. 8a). For a low NMP:water mixture ratio, the modified surfaces were characterized by a homogeneous distribution of uniformly distributed surface features. As the NMP:water mixture ratio increased to [NMP]=60%, a distinct mixture of small and large spherical polymer islands were formed, as noted by AFM imaging. Also, there was a significant increase in RMS surface roughness from $R_{rms}=0.35$ nm at [NMP]=15% to $R_{rms}=0.92$ nm at [NMP]=60%. These findings suggest that the surface morphology of the grafted polymers can be tuned by altering the solvent-substrate wetting properties.

[00101] The effect of NMP on the topology of the high surface density (i.e. polymer feature spacing>50 nm) grafted polymer layers can be conveniently illustrated by inspecting the height histograms of the polymer surface features. As a comparison, the height histograms for the grafted PVP layers formed in NMP/water mixtures of [NMP]=60% and [NMP]=100% at $[M]_0=30\%$ are shown in FIGS. 9a and 9b, respectively. While previous results noted an increased surface roughness for grafting at [NMP]=60% ($R_{rms}=1.52$ nm) compared to [NMP]=100% ($R_{rms}=0.72$ nm), the surface feature height histogram clearly reveals that the grafted polymer surface formed at [NMP]=60% has a bimodal feature height distribution. This may be expected when considering the shape, morphology and height of the polymer surface features imaged by AFM at [NMP]=60% (FIG. 8c) as compared to [NMP]=100%. The bimodal distribution may be characterized by smaller features in the size range below 1 nm and larger clusters in the range of 1-8 nm (FIG. 9a). While smaller features contribute to the overall number density of surface features, larger features that appear as polymer clusters make a disproportionately large contribution to the RMS surface roughness due to the increased diameter or surface area of the features (eq 1). It is hypothesized that the large polymer clusters or aggregates formed as the result of non-uniform surface wetting by the NMP/water mixture solvent. In contrast, grafting in pure NMP resulted in a continuous single mode distribution of surface features height with $S_{skew}=1.12$ (FIG. 9b) relative to skewness of $S_{skew}=3.42$ for grafting at [NMP]=60% (FIG. 9a). The above results demonstrate that 1-vinyl-2-pyrrolidone graft polymerization in pure NMP resulted in a narrower size distribution of tethered chains relative to the NMP/water mixtures.

[00102] These data demonstrate that the topology of the grafted polymer layer can be controlled by the proper selection of reaction conditions and water/NMP mixture composition, thereby enabling a wide-range of potential practical applications.

[00103] Plasma-Induced FRGP Layer Growth of Polystyrene on Silicon. In Ex. 7 and 9, polystyrene was chemically grafted to silicon substrates using a two-step approach consisting of AP plasma surface initiation and free radical graft polymerization (FRGP). Synthesis of

1 polystyrene grafted silicon by plasma surface initiation was confirmed by ATR-FTIR
spectroscopic analysis. With FRGP, monomer initiation by plasma-induced graft
polymerization of styrene occurs by plasma surface initiation and thermal solution initiation.
In the former, monomer initiation is achieved at relatively low reaction temperatures ($T \sim$
5 70°C) by formation of surface radicals by plasma surface treatment, from which monomer
addition can occur. In the latter, monomer decomposition and polymerization in solution ($T \geq 100^{\circ}\text{C}$) results in the formation of macroradicals which may remain in solution or compete
with monomer for grafting to activated surface sites. Therefore, we considered grafted
10 polymer chain growth by both initiation pathways and in the transition regime by studying
grafting at the following conditions: Regime I = 70°C , Regime II = 85°C , and Regime III =
 100°C .

[00104] The grafted polystyrene surface initiator and polymer chain density was dependent
on the plasma processing parameters (i.e., treatment time, RF power, surface conditioning),
as noted earlier, and the surface-bound polymer chain length (i.e., polymer brush thickness)
15 was dependent on the initial monomer concentration and reaction temperature, as described
in the established mechanism for FRGP. Plasma-induced graft polymerization of
polystyrene, over an initial monomer concentration range of 10-50 vol.%, resulted in
maximum layer growth for the M30 grafted silicon, as shown in FIG. 10. Further increase in
initial monomer concentration resulted in a decrease in total layer growth by more than 25%
20 and 50% for the M40 and M50 substrates, respectively.

[00105] Elevated reaction temperatures for M30 in Regime II led to an increase of more
than 3.6 times in grafted polymer layer thickness, attributed to the increased initiation and
grafting efficiency leading to polymer brush layer growth. Graft polymerization for M30 in
Regime III resulted in a 36% decrease in grafted polymer layer thickness, with respect to
25 grafting in Regime II, in addition to layer growth termination within 5 h.

[00106] Thermal initiation of polymer chains in Regime III at 100°C was apparent given
the increase in solution viscosity within a short reaction interval as well as heterogeneous
polymer grafting, which was verified by a substantial increase of $\pm 10\%$ standard deviation in
layer thickness and the presence of visible polymer aggregates on the surface (observed by
30 optical microscope at 10x resolution). The rate of polymer chain growth with reaction time
(FIG. 11) further illustrates the effect of reaction temperature on surface chain propagation
and chain termination. Graft polymerization for M30 in Regime III resulted in more than a
100% increase in the rate of initial surface chain growth (reaction time < 0.5 h) with respect
35 to grafting in Regime I and II (FIG. 11a). However, over a longer reaction period (reaction
time ~ 8 h), the rate of surface chain growth for Regime II was greater than for Regime I and
III, with an initial growth rate of 22.6 \AA/hr for grafting in Regime II.

[00107] Increasing the initial monomer concentration led to a reduction not only in grafted
polymer layer thickness but also in the control of polymer layer growth. Likewise, the initial

1 rate of chain growth ($t = 0.5$ h) for M50 surface grafting increased by more than 10%, 20%,
and 24% for Regime I, II, and III, respectively (FIG. 11b). Also, an observed decrease in the
reaction time interval before the onset of chain termination, with respect to M30 surface
grafting, was noted for each reaction regime. Thus, for Regime I, II, and III, a 1:1 volume
5 ratio of monomer to solvent led to both reduced control of layer growth and total layer
thickness.

[00108] In another embodiment of the invention, the surface density of grafted polymers
can be increased by combining high temperature initiation, to achieve a high surface density
of grafted chains, with low temperature surface polymerization, to reduce polymer grafting
10 and early chain termination. In this manner, a graft polymerization approach described as
Rapid Initiation (RI) was used, by which plasma-treated silicon substrates were graft
polymerized with 30% styrene in chlorobenzene for a short specified time interval at 100°C
(step 1) and then transferred to a separate heating bath at 85°C (step 2) for the remainder of
the reaction time interval. The RI-grafted polymer film growth demonstrated a unique
15 dependence on the step 1 time interval (t_{s1}), measured by the layer thickness observed after
the step 2 time interval (t_{s2}) (FIG. 12). An increase in t_{s2} layer thickness of 38% was observed
when t_{s1} was increased from 5-15 min, as expected by the rate of polymerization and
fractional coverage of surface initiation sites achieved for a longer exposure to a high reaction
temperature. The maximum t_{s1} polymer layer thickness was observed at 15 min, and a 30%
20 decrease in t_{s2} layer thickness was observed when t_{s1} was increased to 30 minutes. The RI-
grafted polymer film growth at $t_{s1} = 15$ min exhibited similar polymer layer growth behavior
in comparison to graft polymerization of 30% (v/v) styrene in chlorobenzene at 85°C, with
quasi-linear layer growth over a period of 20 hours. Also, the polymer film thickness after an
interval of 20 h increased by 25% (FIG. 13), as expected by the increase in the initial rate of
25 surface grafting.

[00109] Atomic Force Microscopy (AFM) was used to image and compare the nanoscale
features of the polystyrene layers that were graft polymerized in Regime I, II and III (FIG.
14). Tapping mode AFM of polymer surface features in air allowed for an analysis of the
surface feature density, feature height and diameter (i.e., chain length) and the spatial
30 distribution of features in a $1 \times 1 \mu\text{m}$ area. The increase in initial monomer concentration
from M30 to M50 in Regime I and Regime II demonstrated both an increase in surface
feature density and the average feature size. M50 grafted surfaces in Regime I resulted in a
uniformly dispersed, dimpled feature morphology with lateral feature size in the range of 30-
40 nm and more than 100% increase in the RMS surface roughness (R_{rms} , eq 1) compared to
35 M30 surface grafting in Regime I. Similarly, comparison of M30 and M50 grafted surfaces
in Regime II evidenced a similar increase in R_{rms} from 0.55 to 1.11 nm with average feature
sizes in the range of 15-25 to 50-60 nm, respectively. However, it is important to note that,
when the monomer concentration was increased to M50 in Regime II, the presence of

1 heterogeneously dispersed, large globular grafted polymer features commingled with smaller
 5 polymer surface features was observed by AFM (FIG. 14d). The seemingly random and
 asymmetrical arrangement of surface features is attributed to polymer grafting of chains
 formed in solution, as a result of high monomer concentration initiated by fragmented
 10 initiator species from the surface. The AFM studies for the M50 surfaces confirm previous
 observations in Regime II of a decrease in the apparent rate coefficient and less controlled
 layer growth, with termination occurring at shorter time intervals relative to the M30
 surfaces. Polystyrene grafted M30 surfaces in Regime III resulted in more than a 3 fold
 15 increase in R_{rms} with respect to layers grafted in Regime II (FIG. 14e), and were composed of
 large surface features with lateral feature dimensions of 70-90 nm. However, for M50
 surfaces grafted in Regime III, plasma surface initiation combined with thermal solution
 initiation at elevated monomer concentration resulted in the formation of heterogeneous
 20 layers composed of continuous peaks and valleys, presumably a result of chain grafting from
 solution. The poor quality of the grafted layers, with limited control of grafted polymer layer
 growth, suggests that these grafted layers would not be suitable for applications that required
 25 a high level of surface uniformity.

[00110] Plasma-Induced NMGP Layer Growth. In Ex. 8, controlled nitroxide-mediated
 20 graft polymerization (NMGP) studies were conducted using 2,2,6,6-tetramethyl-1-
 piperidinyloxy radical (TEMPO) to reversibly cap polymer chains growing both in solution
 and from the surface, thereby preventing uncontrolled polymerization. Controlled radical
 25 polymerization, noted by the linear increase in grafted layer thickness with time, was
 achieved by graft polymerization of M50 surfaces at 120°C in the presence of TEMPO at [T]
 = 10 mM to yield a polystyrene brush layer thickness of 283.4 Å. The kinetic growth curves
 of NMGP with addition of TEMPO ([T] = 5-15 mM) are shown in FIG. 15. Increased
 30 control of surface grafting was achieved by increasing the concentration of TEMPO from 5 to
 10 mM, as noted by a 35% increase in total polymer layer growth, as shown in Table 5.

Table 5

30	[TEMPO] (mM)	Polymer Film Thickness (Å) ^(a)	Water Contact Angle (°)
5	5	210.4 ± 1.2	90.0
35	7	219.1 ± 2.7	90.0
	10	283.4 ± 2.2	90.0
	15	189.9 ± 1.9	90.0

(a) Total polymer film thickness measured by ellipsometry at final data point.

[00111] Further addition of TEMPO did not alter the behavior of the linear layer growth but significantly reduced the total layer growth. The decrease in layer growth with increased TEMPO is presumably a direct result of the equilibrium shift towards the dormant phase, thus increasing the frequency of chain capping and reducing the growth of radical polymer chains in solution.

[00112] The effect of reaction temperature for NMGP was illustrated by a non-linear dependence over a temperature range of T = 100-130°C, as shown in Table 6.

10 Table 6

Temperature (°C)	Polymer Film Thickness (Å) ^(a)
100	38.1 ± 6.6
110	53.4 ± 6.7
120	283.4 ± 2.2
130	125.2 ± 2.5

^(a) Total polymer film thickness measured by ellipsometry at final data point.

[00113] Atomic Force Microscopy was used to image the topology of the NMGP polymer grafted layers (FIG. 16) and to elucidate the contribution of surface feature size in the height histogram (FIG. 17). The AFM images of the NMGP polymer layer were characterized by a spatially homogeneous, highly dense grafted polymer phase with features of uniform surface height represented by an R_{rms} of 0.36 nm, nearly 80% less than for the M30 grafted surface in Regime II ($R_{rms} = 1.70$ nm). In fact, the uniformity of surface feature height for the controlled polystyrene grafted layer remarkably resembled that of the native silicon surface ($R_{rms} \approx 0.20$ nm). The height histogram data illustrated in FIG. 14 suggested a highly uniform polymer feature height distribution, as confirmed by the skewness of the height distribution that approached zero with a characteristic width of the Gaussian distribution of $\omega = 1.3$ nm. In comparison to other controlled “living” free radical graft polymerization methods, an RMS surface roughness of 0.7 nm was reported for “living” surface initiated anionic graft polymerization of polystyrene to silicon. Also, the surface topology anionic graft polymerized polystyrene, as illustrated by AFM imaging, suggested a dendritic structure with “hole” defects ranging in size from 0.2-0.3 μm in diameter and 11-14 nm in depth, uniformly

1 dispersed throughout the layer. The rationale provided by the author for the defect
morphology was due to the low grafting density on the silicon surface. Therefore, it may be
concluded that the current method for NMGP on silicon, in comparison to other FRGP or
“living” controlled polymerization methods, not only achieved a high fractional surface
5 density of grafted polymers due to plasma surface initiation, but also demonstrated controlled
polymerization in the presence of TEMPO with 1) linear layer growth with respect to time, 2)
a decreased RMS surface roughness and 3) a decreased height distribution skewness.

[00114] In the absence of the TEMPO control agent, kinetic growth of polymer layers by
10 plasma-induced FRGP demonstrated a maximum layer thickness for surface grafting at 30
vol.% monomer concentration at 85°C. Increasing both the reaction temperature (T = 100°C)
and monomer concentration (50 vol.%) led to an increased initial growth rate but a reduced
polymer layer thickness, due to uncontrolled thermal initiation and polymer grafting from
15 solution. AFM images of grafted polystyrene layers confirmed the kinetic growth data with
highly uniform surface grafting at low monomer concentration and reaction temperature and
heterogeneous, globular surface feature formation at high monomer concentration and
reaction temperature. Surface grafting by controlled NMGP exhibited linear kinetic growth
with respect to time and surfaces imaged by AFM were characterized by a low surface
20 roughness with a uniform distribution of surface feature heights.

[00115] Tapping mode 3-D surface renderings of examples 2-4, 6, and 10 of the invention
are provided in FIGS. 20-25. For comparison, FIGS. 18 and 19 are 3-D surface renderings of
silicon and silylated silicon, respectively, prior to plasma treatment.

25 [00116] The present invention has been described with reference to exemplary
embodiments and aspects, but is not limited thereto. Persons skilled in the art will appreciate
that other modifications and applications can be made without meaningfully departing from
the invention. Accordingly, the description should be read consistent with and as support for
30 the following claims, which are to have their fullest and fairest scope, both literally and under
the doctrine of equivalents.

[00117] Throughout the text and the claims, use of the term "about" in relation to a range
of values is intended to modify both the high and low values recited, and reflects the
penumbra of variation associated with measurement, significant figures, and
35 interchangeability, as understood by a person having ordinary skill in the art to which this
invention pertains.

1 [00118] This application is based on and claims priority of U.S. provisional patent
application number 60/857,874, filed November 10, 2006, the entire contents of which are
incorporated by reference herein.

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1 What is claimed is:

1. A method of modifying a substrate surface by plasma-induced graft polymerization, comprising:

5 treating a substrate surface with (a) an atmospheric pressure (AP) plasma and (b) an ethylenically unsaturated monomer or monomer solution.

10 2. A method as recited in claim 1, wherein the substrate comprises an inorganic substrate.

15 3. A method as recited in claim 2, wherein the inorganic substrate comprises an elemental material selected from the group consisting of silicon, aluminum, hafnium, zirconium, titanium, iron and gold.

20 4. A method as recited in claim 3 wherein the inorganic substrate comprises a silicon wafer.

25 5. A method as recited in claim 2, wherein the inorganic substrate comprises an inorganic oxide.

6. A method as recited in claim 5, wherein the inorganic oxide is selected from the group consisting of silica, alumina, hafnia, zirconia, and titania.

7. A method as recited in claim 2, wherein the inorganic substrate comprises a metallic or ceramic material capable of supporting formation of surface oxides, hydroxides, peroxides, 25 or other functional groups capable of initiating polymerization of an unsaturated monomer.

8. A method as recited in claim 1, wherein the substrate comprises a vinyl-functionalized substrate.

30 9. A method as recited in claim 1, wherein the substrate comprises a polymeric substrate.

10. A method as recited in claim 9, wherein the polymeric substrate comprises an organic polymer.

35 11. A method as recited in claim 10, wherein the organic polymer is selected from the group consisting of polystyrene, polyamides, and polysulfones.

1 12. A method as recited in claim 9, wherein the polymeric substrate comprises an
inorganic polymer.

5 13. A method as recited in claim 1, wherein the substrate comprises an inorganic substrate
having a polymeric layer adsorbed thereon.

· 14. A method as recited in claim 1, wherein the substrate comprises a dendritic substrate.

· 15. A method as recited in claim 1, wherein the substrate comprises a Langmuir-Blodgett
10 film.

16. A method as recited in claim 1, wherein the substrate comprises a thiol or a silylated
layer.

15 17. A method as recited in claim 1, wherein the AP plasma is formed from a precursor gas
selected from the group consisting of hydrogen, oxygen, nitrogen, air, ammonia, argon,
helium, carbon dioxide, H₂O, methane, ethane, propane, butane, and mixtures thereof.

20 18. A method as recited in claim 17, wherein the precursor gas is carried by a carrier gas.

19. A method as recited in claim 1, wherein plasma treatment is carried out over about a 5
to 120 second time period and at a RF power of from about 20 to 60 W using a hydrogen
plasma.

25 20. A method as recited in claim 1, wherein plasma treatment is carried out over about a
10 second time period and at a RF power of about 40 W.

30 21. A method as recited in claim 1, further comprising cleaning the substrate and
conditioning it in a humidity chamber for a desired length of time prior to treating it with an
AP plasma.

22. A method as recited in claim 21, wherein conditioning the substrate results in
formation of a layer of adsorbed water on the substrate.

35 23. A method as recited in claim 22, wherein the layer of adsorbed water is substantially a
molecular monolayer.

1 24. A method as recited in claim 1, wherein the at least one ethylenically unsaturated monomer comprises a vinyl or divinyl monomer.

5 25. A method as recited in claim 1, wherein the ethylenically unsaturated monomer comprises an acid vinyl monomer, acrylic or methacrylic ester, polar vinyl monomer, or non-polar vinyl monomer.

10 26. A method as recited in claim 25, wherein the acid vinyl monomer comprises acrylic acid or methacrylic acid.

15 27. A method as recited in claim 25, wherein the ethylenically unsaturated monomer comprises 1-vinyl-2-pyrrolidone.

20 28. A method as recited in claim 25, wherein the ethylenically unsaturated monomer comprises styrene.

25 29. A method of modifying a substrate surface, comprising:
treating a substrate surface with (a) an atmospheric pressure (AP) plasma and (b) a monomer solution.

30 30. A method as recited in claim 29, wherein the monomer solution comprises up to 50% by volume monomer.

35 31. A method as recited in claim 29, wherein the monomer solution includes at least one monomer and at least one solvent, and both the monomer(s) and the solvent(s) are polar.

40 32. A method as recited in claim 29, wherein the monomer solution includes at least one monomer and at least one solvent, and both the monomer(s) and the solvent(s) are non-polar.

45 33. A method as recited in claim 29, wherein the monomer solution has a sufficiently low contact angle with the substrate to wet the surface of the substrate.

50 34. A method as recited in claim 29, wherein the monomer solution includes a solvent selected from the group consisting of N-methyl pyrrolidone, water, and mixtures thereof.

55 35. A method of modifying a substrate surface, comprising:
forming active sites on a substrate surface by directing an atmospheric pressure (AP) plasma at the substrate; and

1 forming graft polymers bound to the substrate surface by contacting the active sites
with a monomer or monomer solution.

36. A method as recited in claim 35, wherein the AP plasma is provided by a plasma jet.

5 37. A method as recited in claim 35, wherein the graft polymers are grown by free radical
· graft polymerization.

10 38. A method as recited in claim 35, wherein the graft polymers are grown by controlled
radical polymerization.

39. A method as recited in claim 35, wherein the graft polymers are grown in the presence
of a free-radical molecule.

15 40. A method as recited in claim 39, wherein the free-radical molecule comprises a
TEMPO free-radical molecule.

41. A method as recited in claim 35, wherein the graft polymers collectively have
polydisperse chain lengths, with $pI \geq 2$.

20 42. A method as recited in claim 35, wherein the graft polymers collectively have
substantially uniform chain length, with $pI < 1.5$.

43. A method of forming a polymer film and anchoring it to a substrate, comprising:

25 (a) providing a clean surface of a substrate;

(b) conditioning the clean surface by removing a native oxide layer, if present, from
the substrate;

(c) forming a layer of adsorbed water on the substrate;

(d) generating a plasma at substantially atmospheric pressure from a plasma

30 precursor gas;

(e) forming polymer initiation sites on the substrate by directing the plasma onto the
surface of the substrate; and

(f) forming a polymer film comprising a plurality of polymer molecules that are
covalently bonded to the substrate by contacting the polymer initiation sites with a monomer
35 or monomer solution.

44. A method as recited in claim 40, further comprising washing the polymer film in a
solvent to remove adsorbed, unbound polymers.

1

45. A method of modifying a substrate surface by plasma-induced graft polymerization, comprising:

5 treating a substrate surface with (a) an atmospheric pressure (AP) plasma and (b) an ethylenically unsaturated monomer or monomer solution;

 wherein plasma treatment time, radio frequency (RF) power, plasma source, plasma precursor gas(es), plasma carrier gas(es) and/or applied voltage are adjusted to maximize formation of surface initiation sites.

10 46. A method as recited in claim 45, wherein the substrate is plasma treated for about 10 s at an RF power of about 40 W.

15 47. A method of modifying a substrate surface by plasma-induced graft polymerization, comprising:

 treating a substrate surface having a layer of adsorbed water thereon with (a) an atmospheric pressure (AP) plasma and (b) an ethylenically unsaturated monomer or monomer solution;

20 wherein formation of surface peroxide initiation sites by plasma treatment is maximized with respect to the amount of adsorbed water on the substrate surface.

25 48. A method as recited in claim 47, wherein the amount of adsorbed water is substantially a molecular monolayer.

30 49. A method as recited in claim 47, the substrate surface is treated with a hydrogen plasma for about 10s at an RF power of about 40 W.

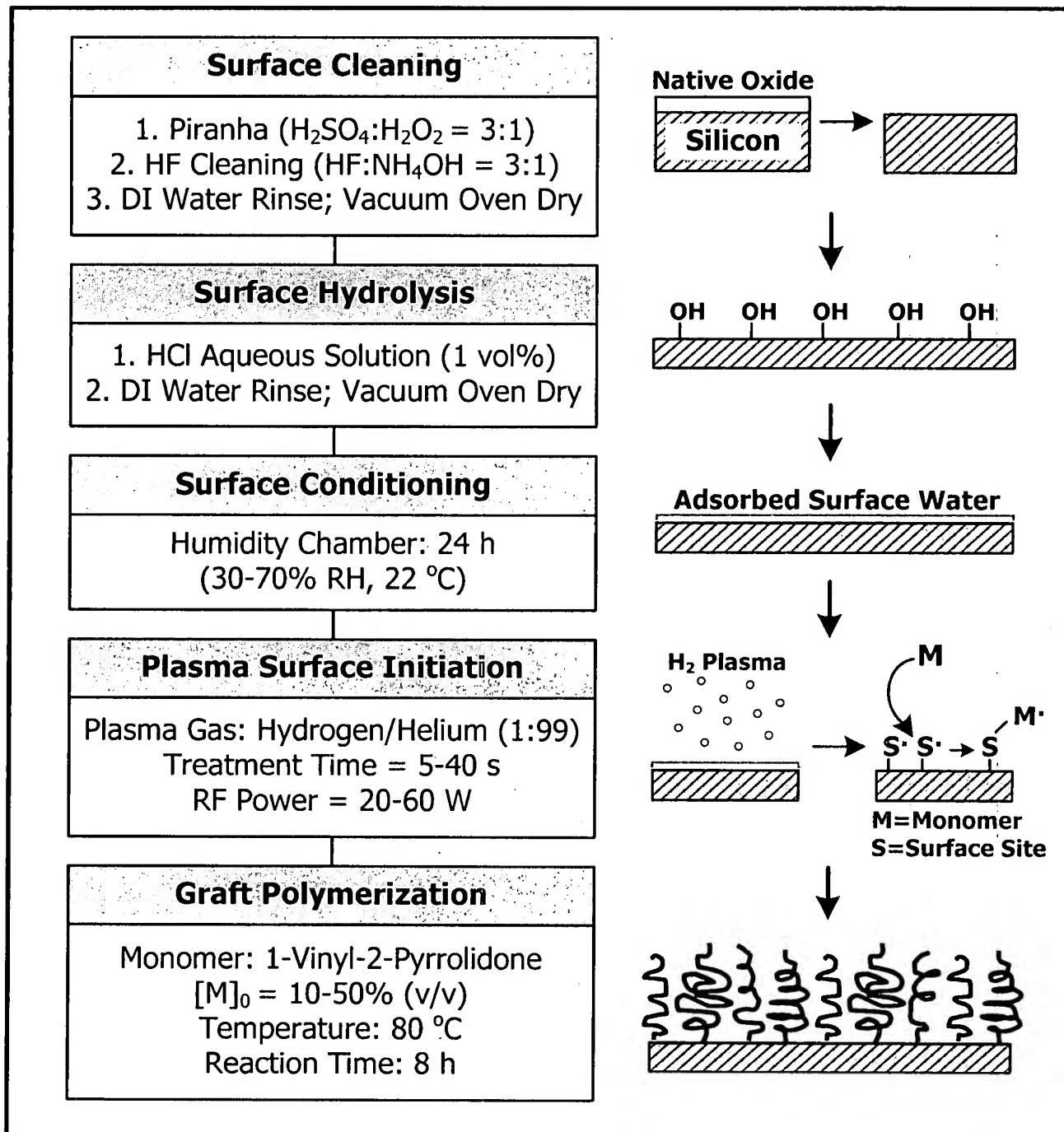
50. A method of modifying a substrate surface by plasma-induced graft polymerization, comprising:

 forming a plasma-treated substrate surface by treating a substrate surface with an atmospheric pressure (AP) plasma; and

 causing graft polymer chains to grow from the substrate surface by contacting the plasma-treated substrate surface with an ethylenically unsaturated monomer or monomer solution for a first time interval, t_1 , at a first temperature T_1 , followed by a second time interval, t_2 , at a second temperature T_2 , where $t_1 < t_2$ and $T_1 > T_2$.

35

51. An inorganic or organic substrate having a surface modified by atmospheric pressure plasma-induced graft polymerization according to the method recited in any one of claims 1-49.

**FIG. 1**

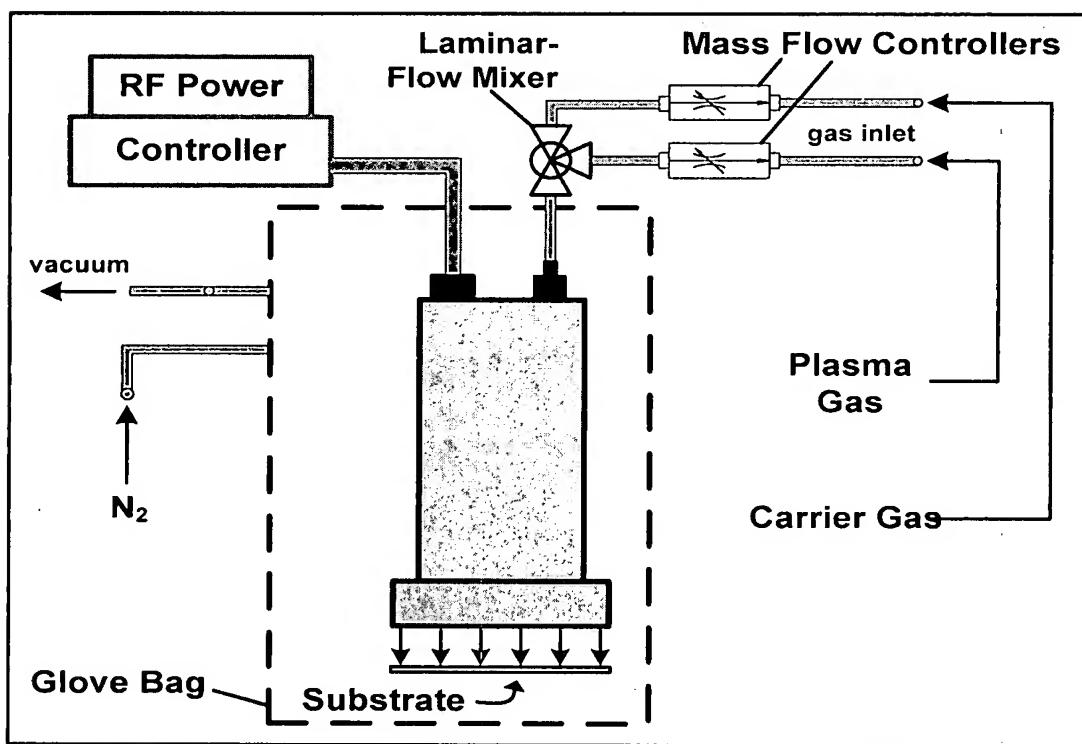
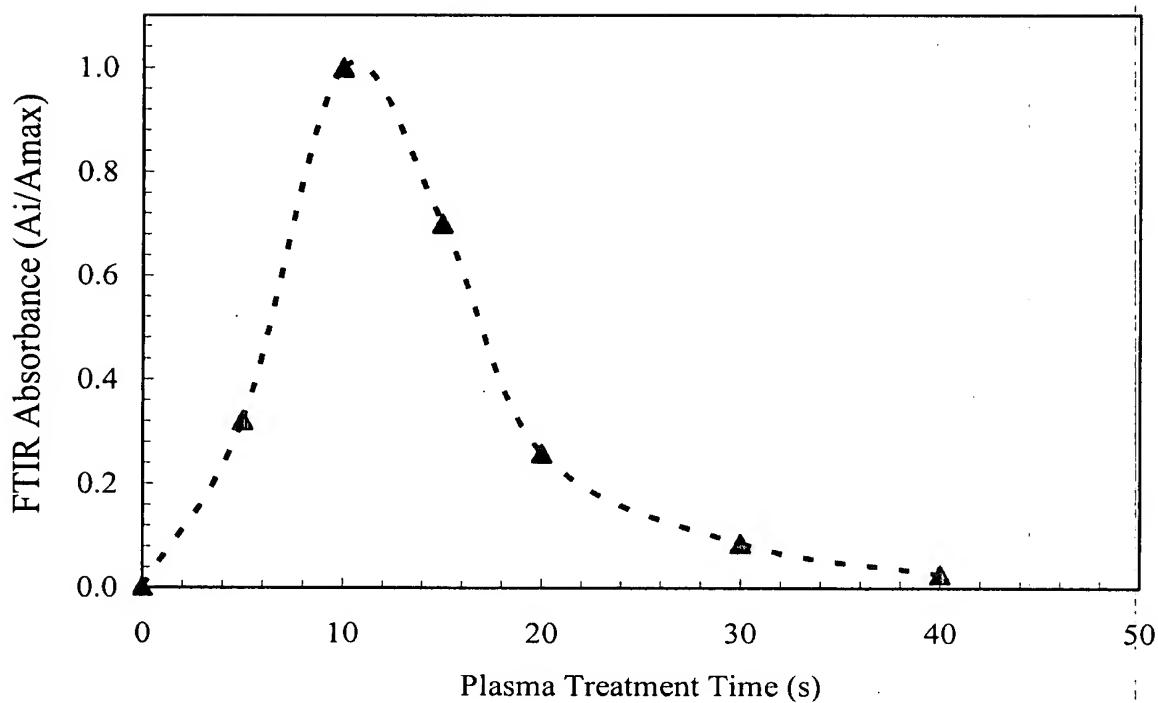
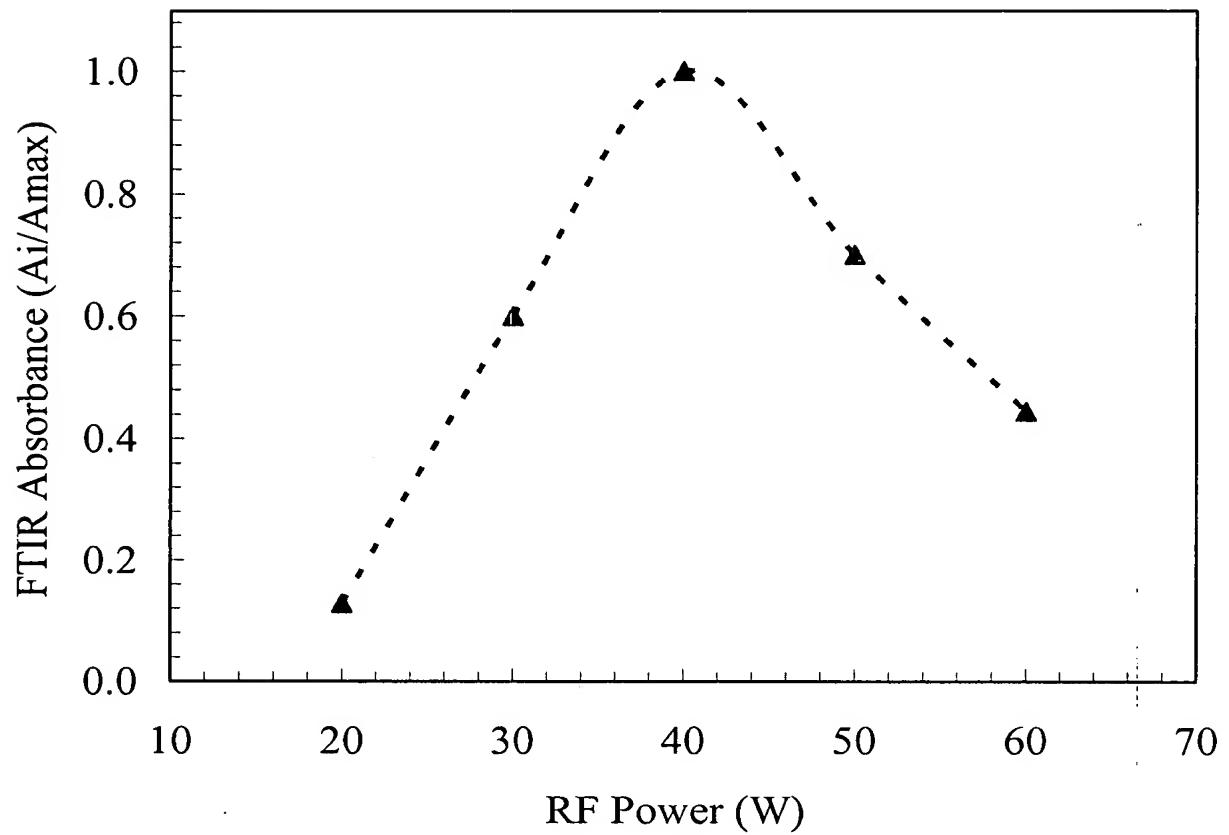


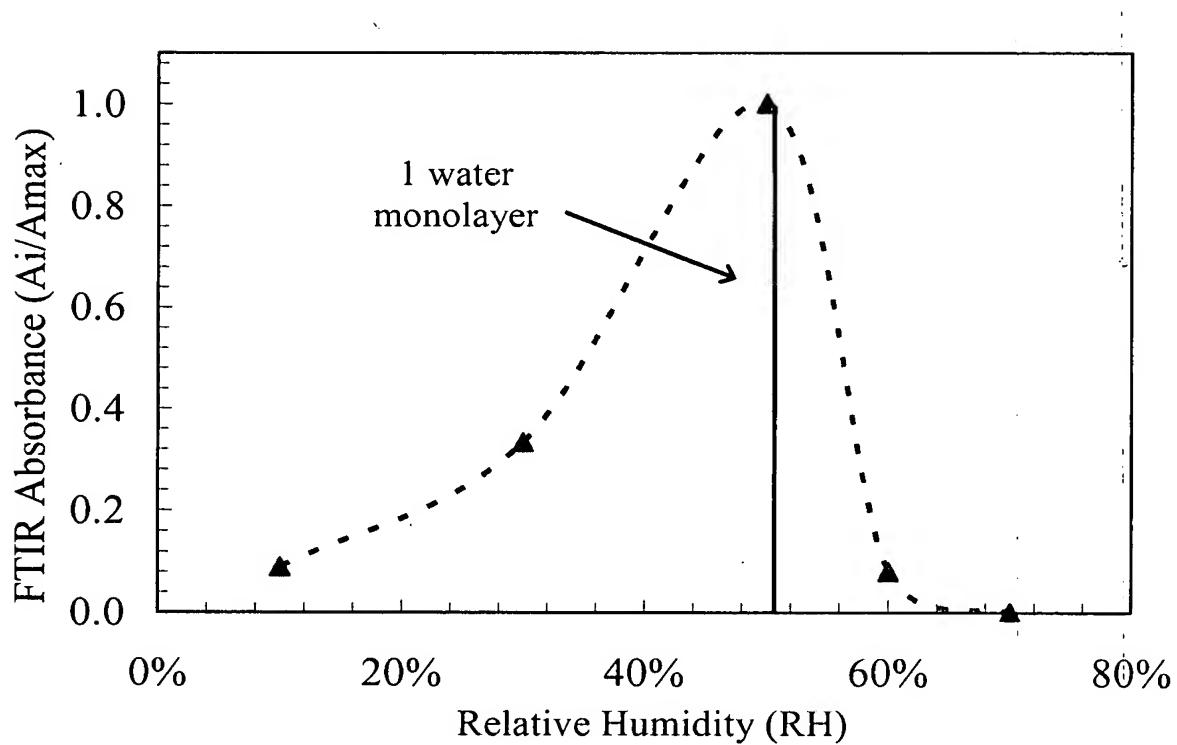
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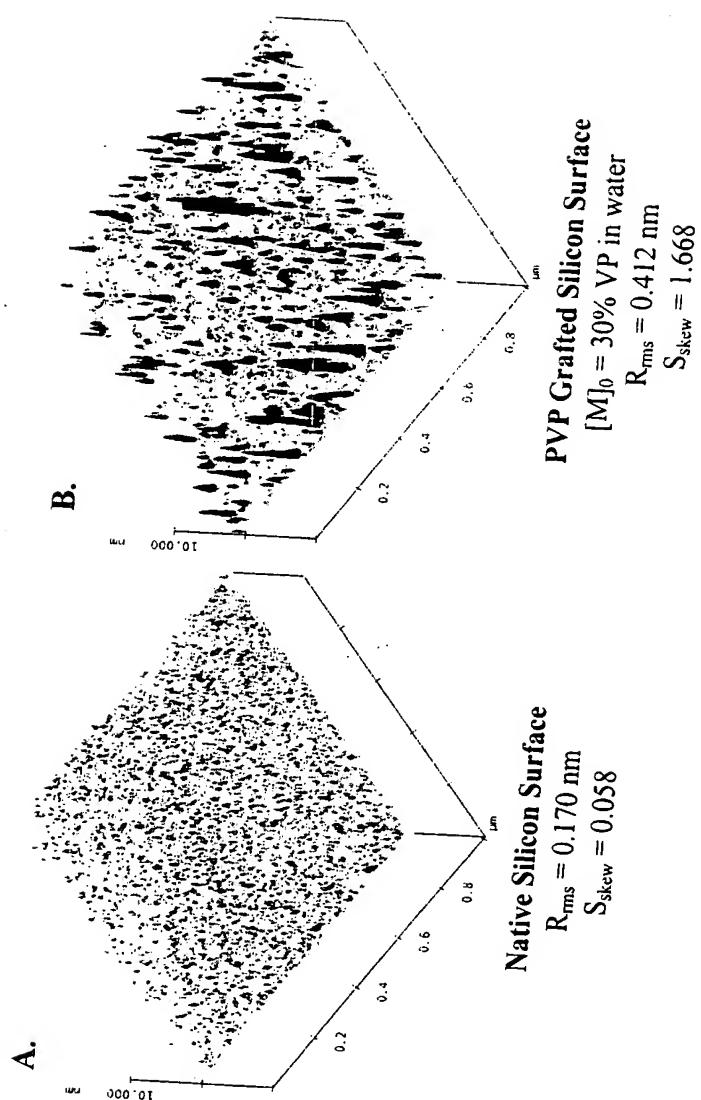
3/25

**FIG. 3**

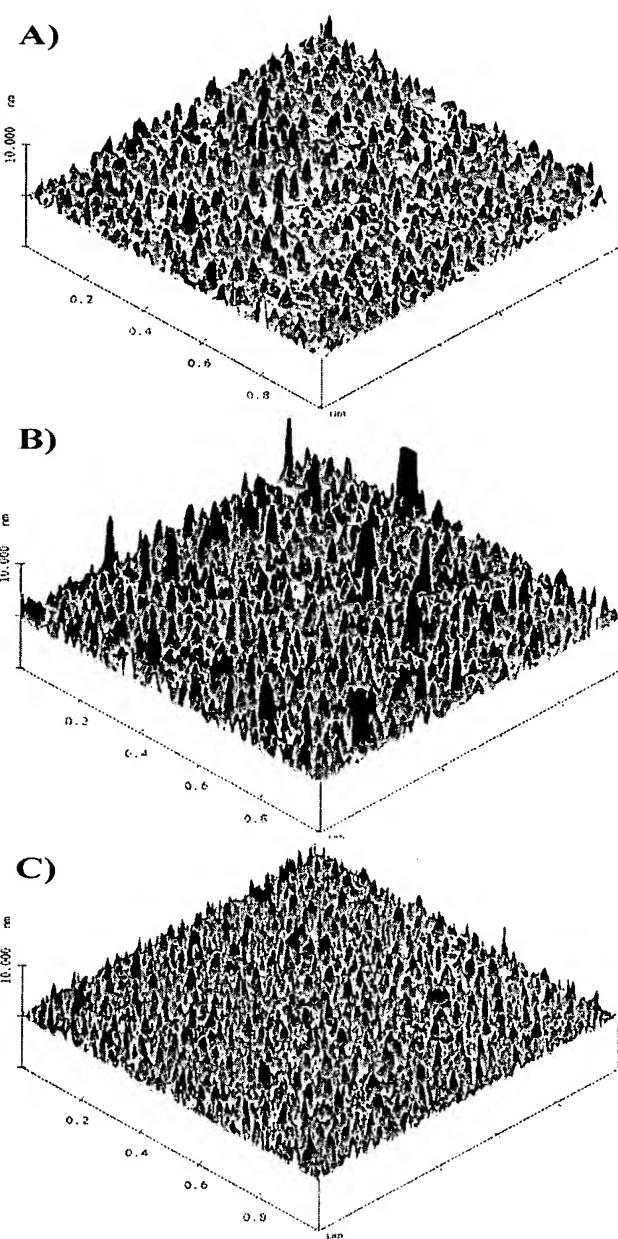
4/25

**FIG 4**

**FIG. 5**

**FIG. 6**

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**FIG. 7**

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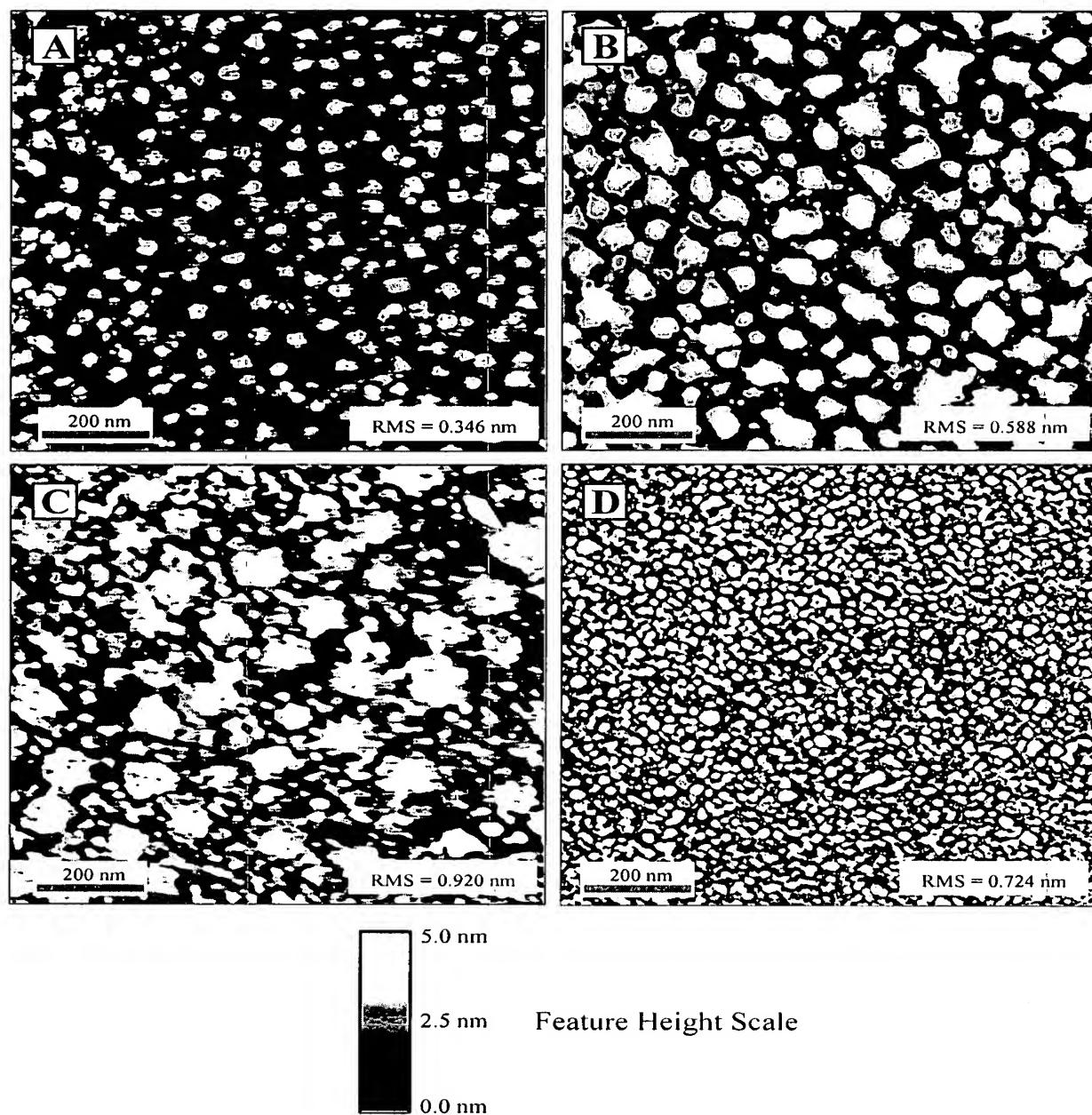
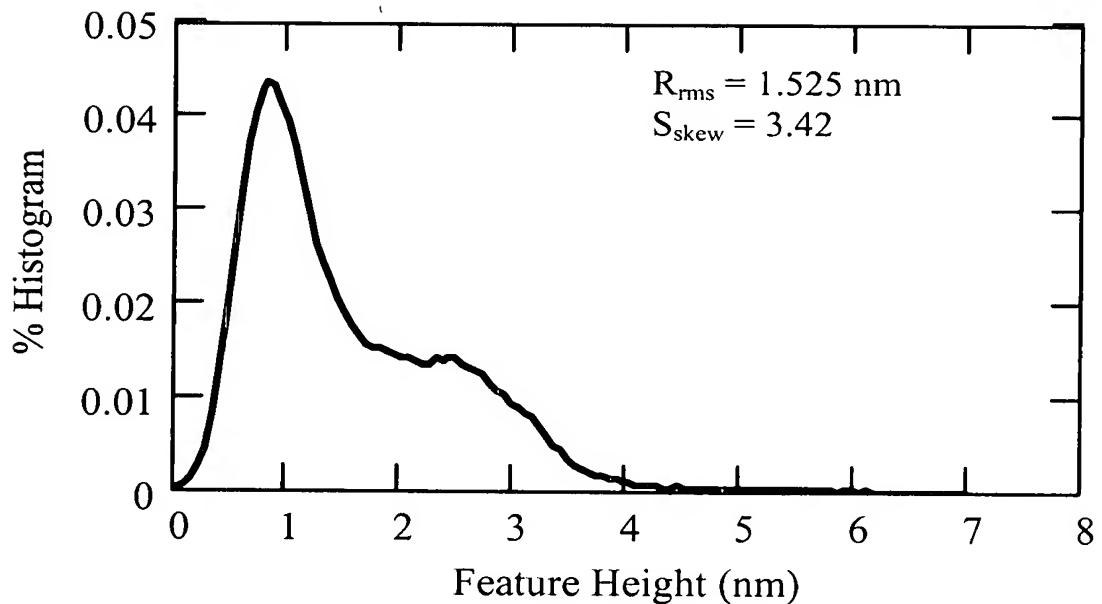
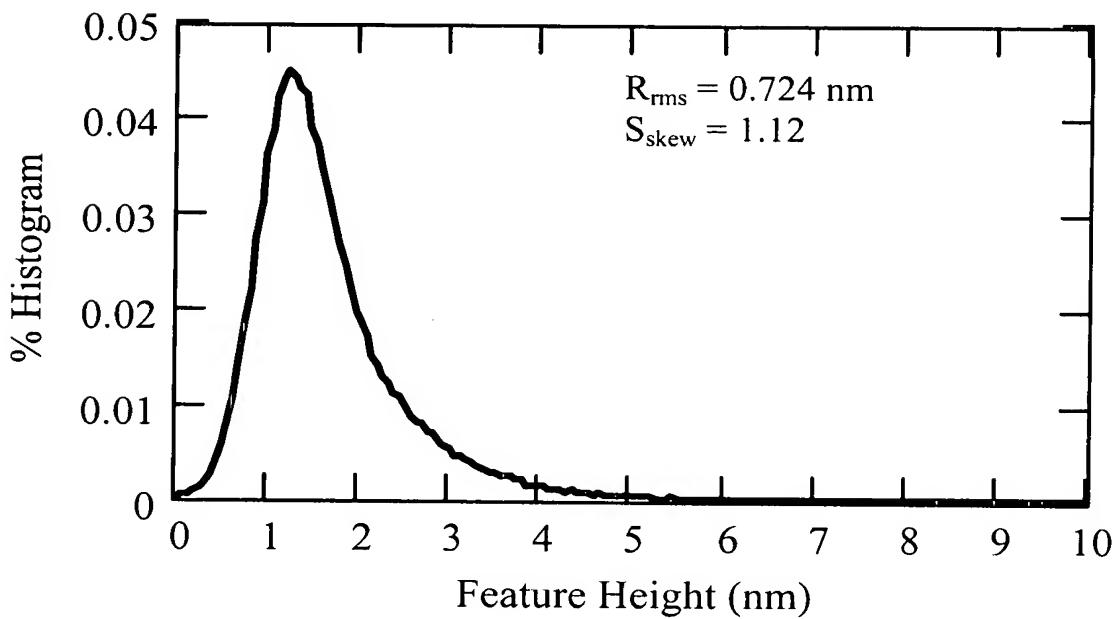
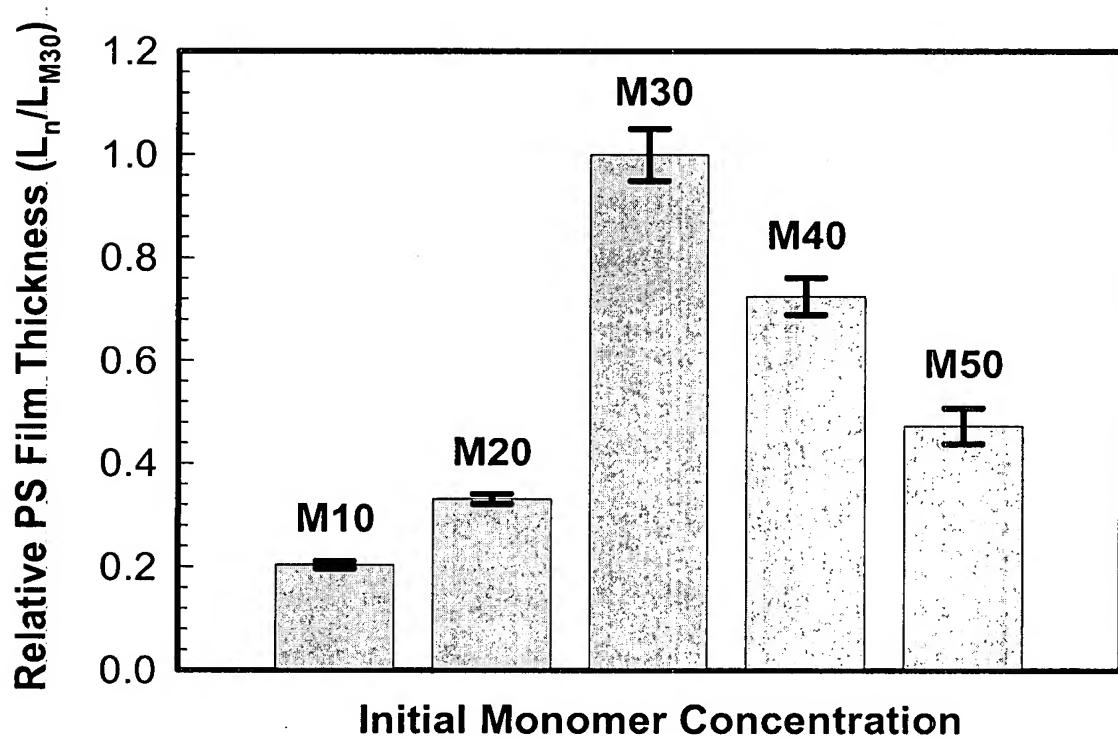


FIG. 8

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**B)****FIG. 9**

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**FIG. 10**

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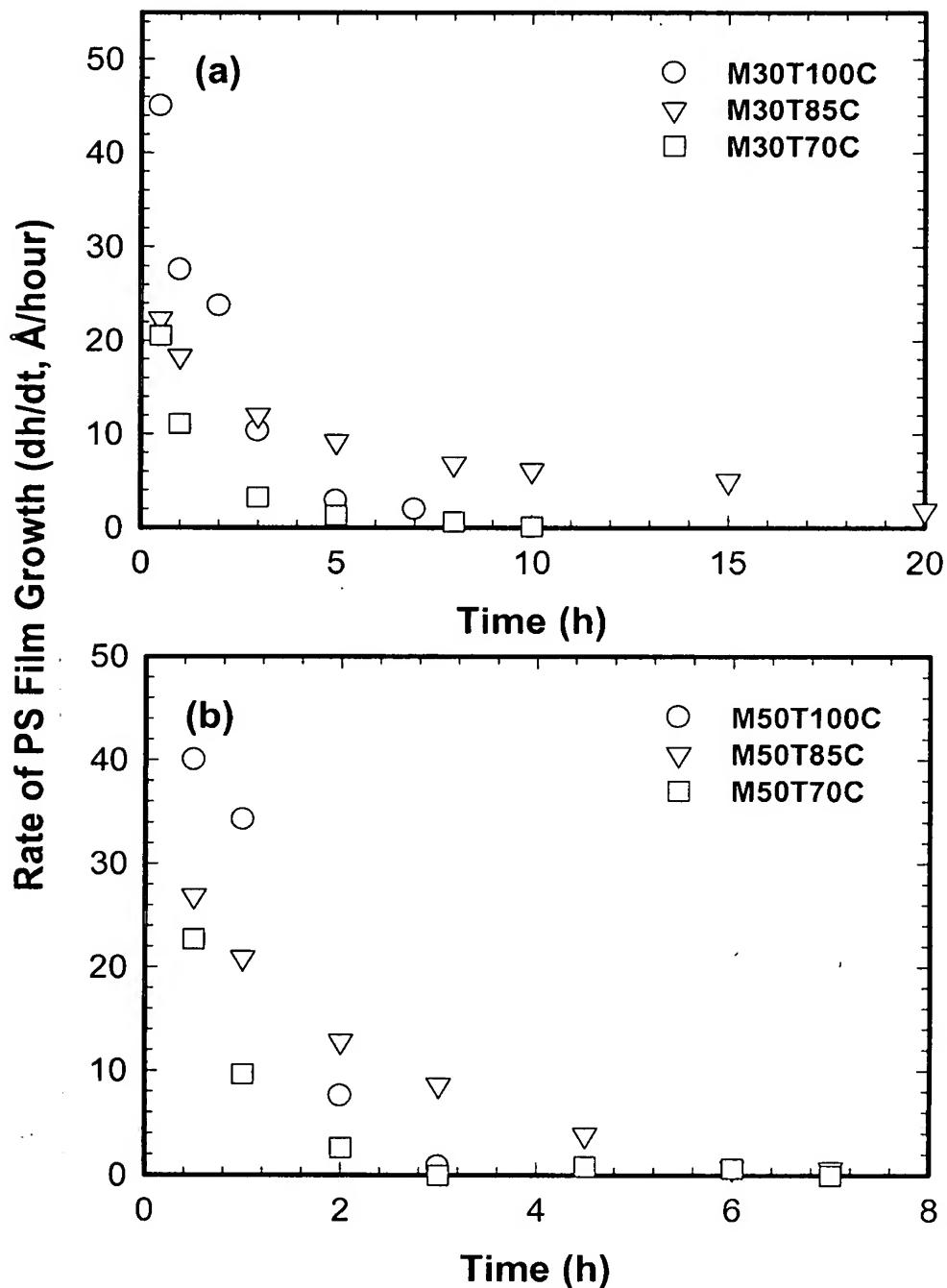
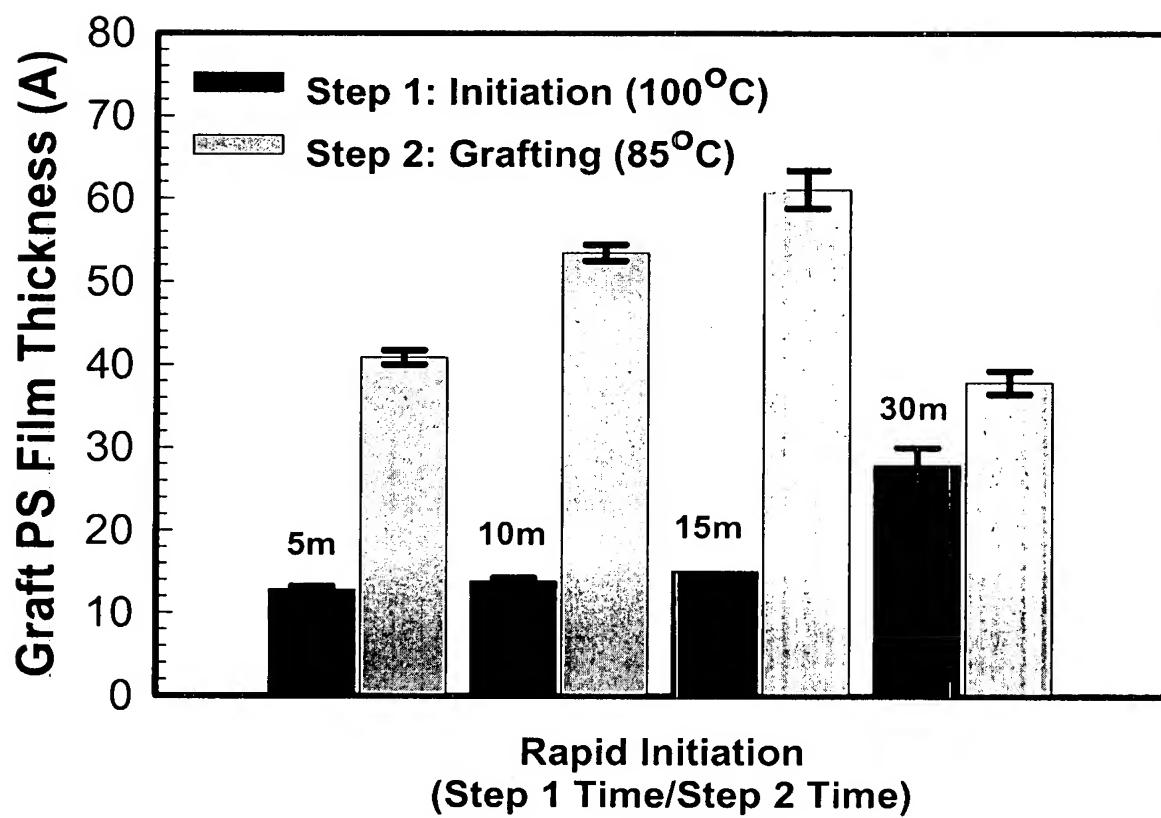


FIG. 11

**FIG. 12**

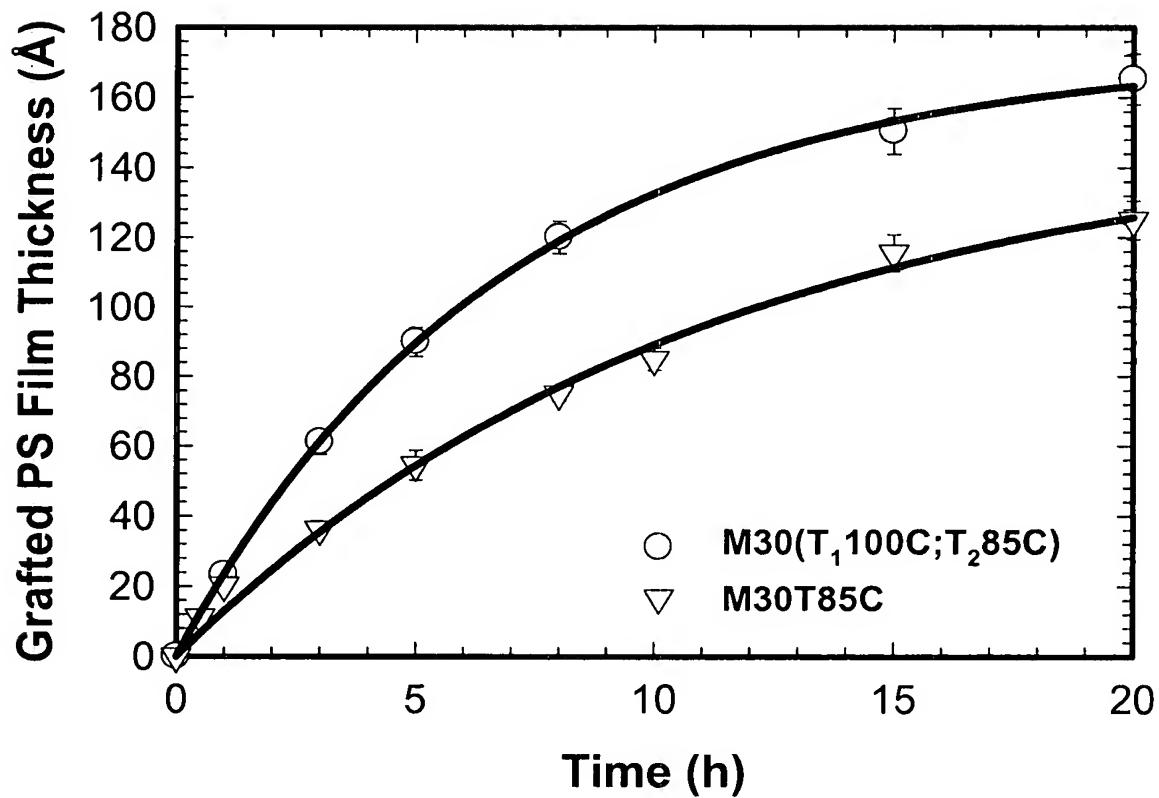
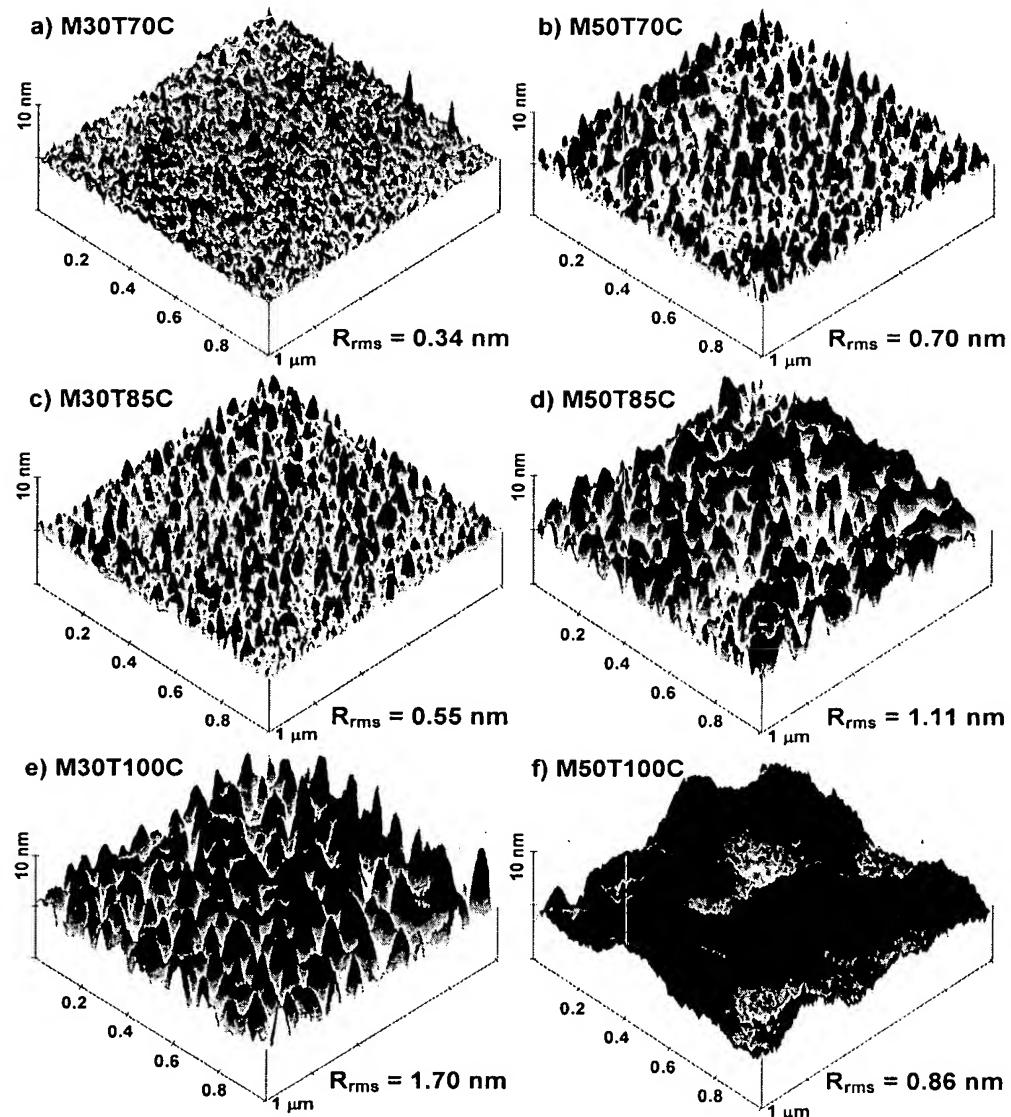


FIG. 13

**FIG. 14**

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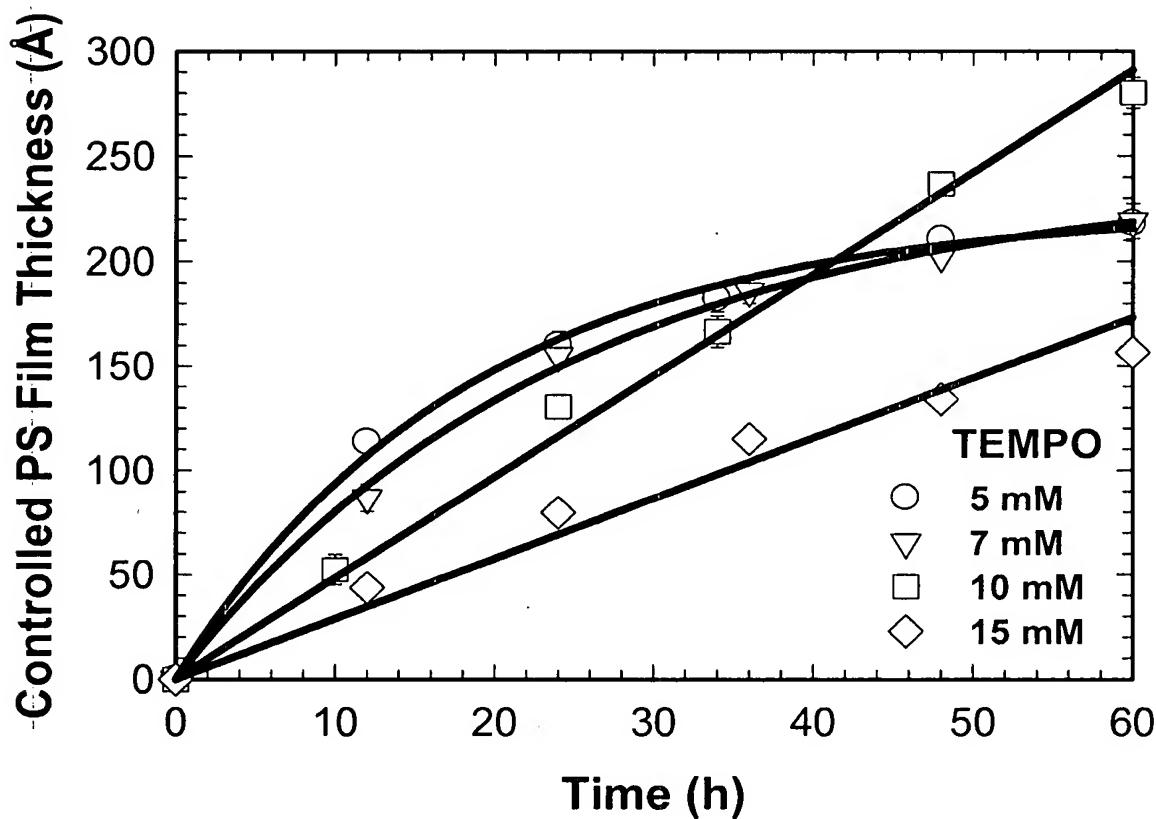


FIG. 15

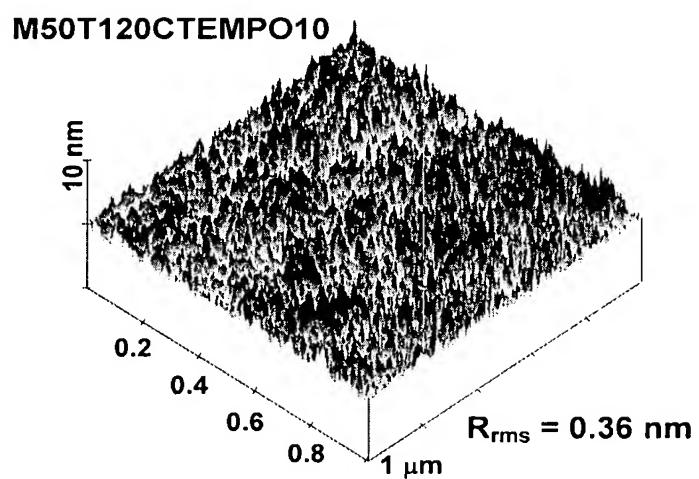


FIG. 16

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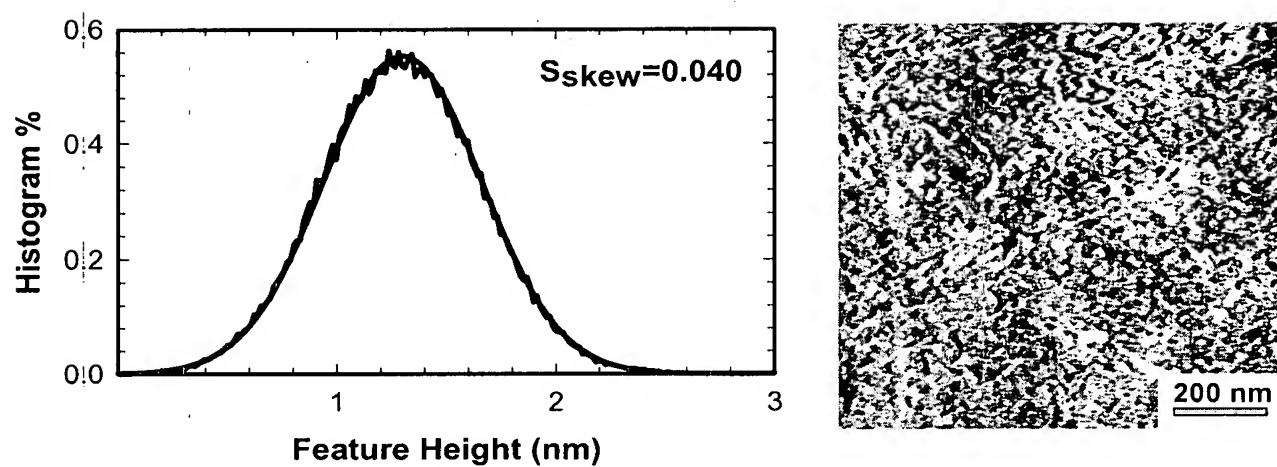


FIG. 17

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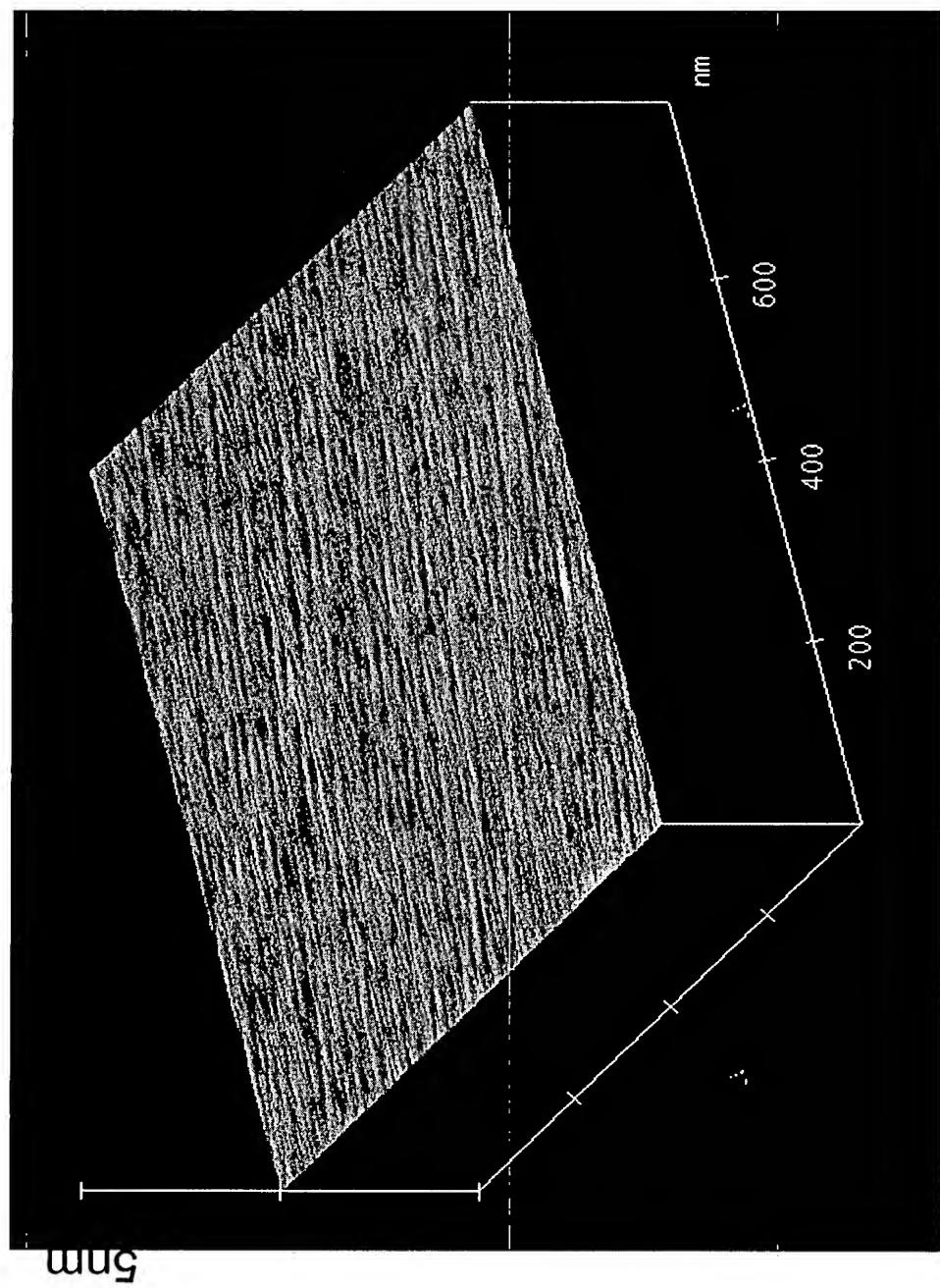


FIG. 18

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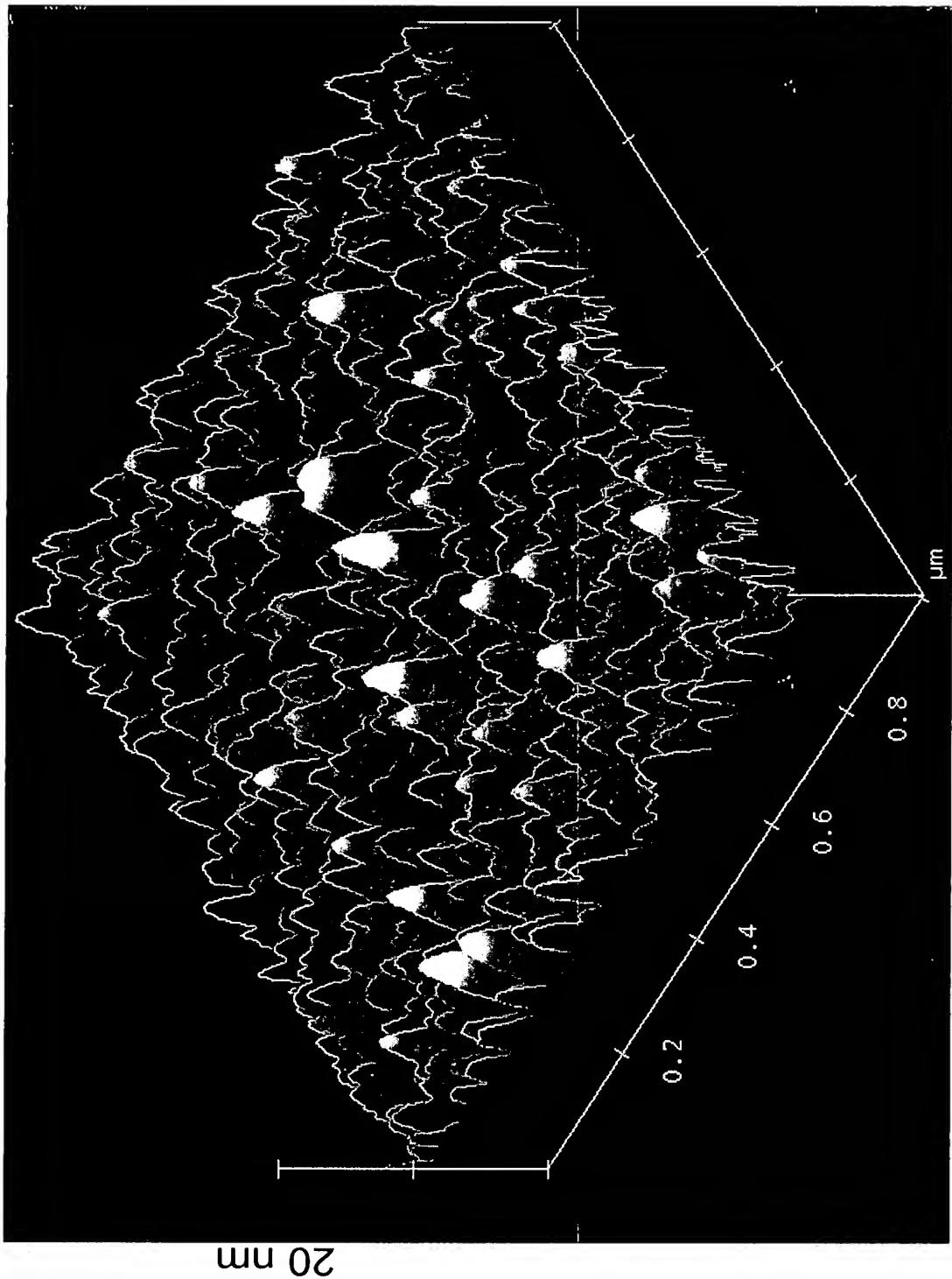


FIG. 19

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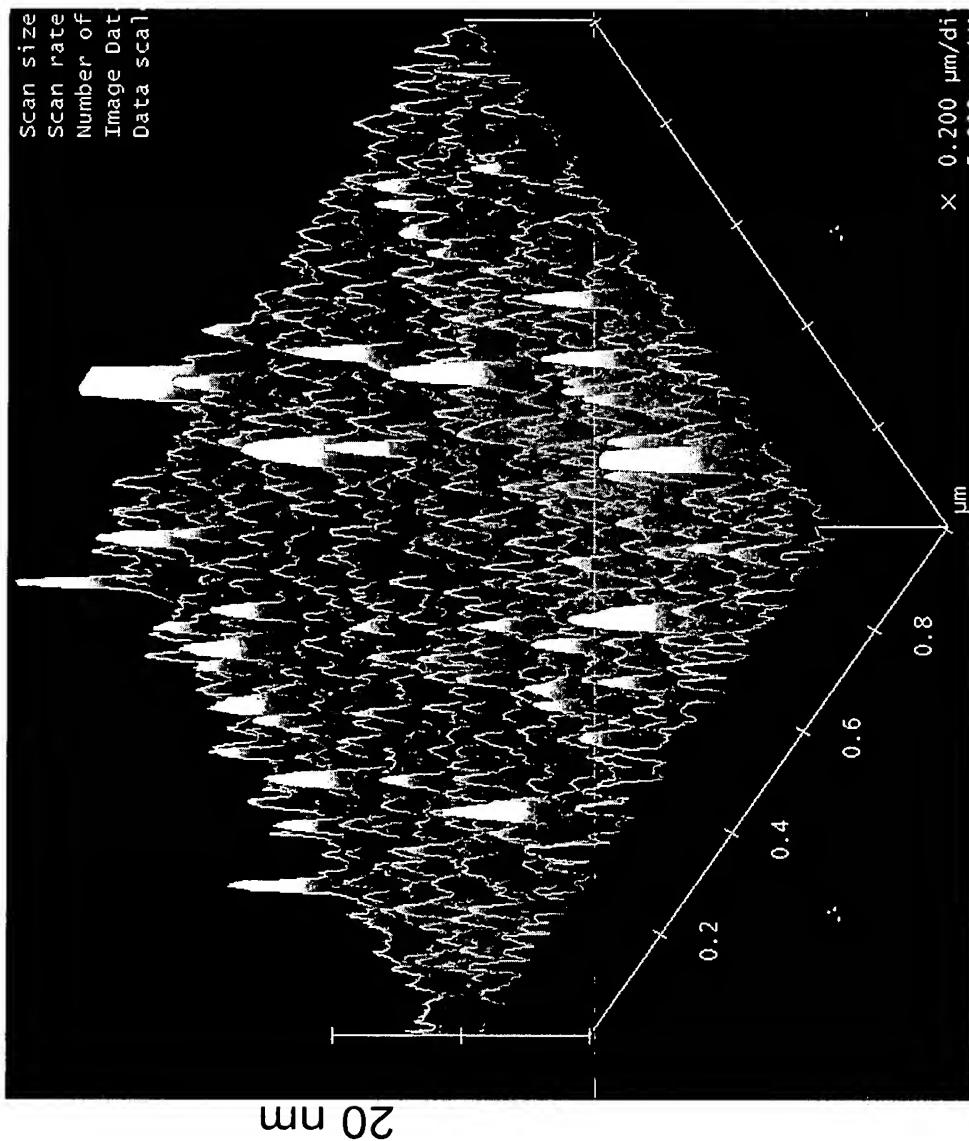


FIG. 20

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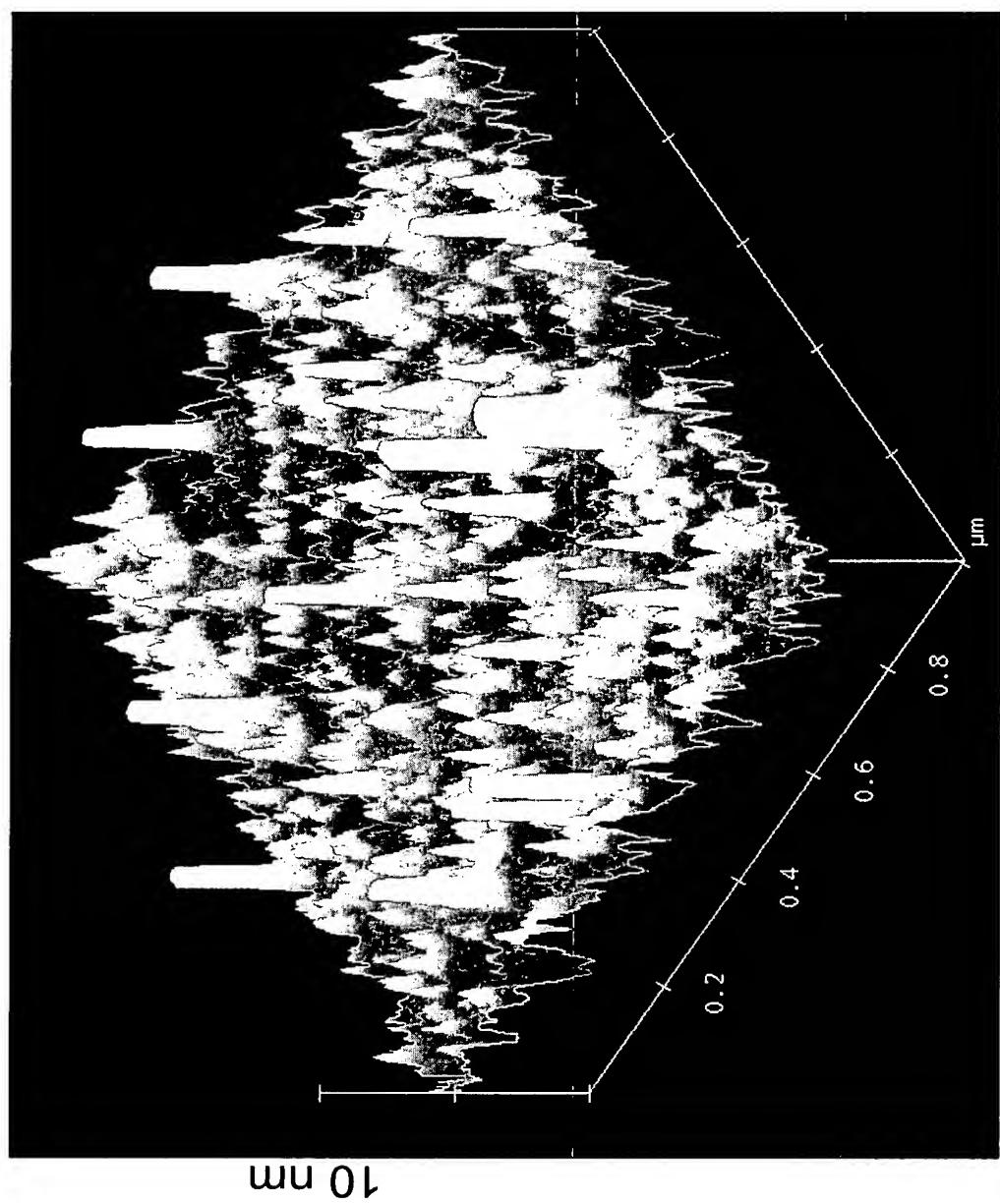


FIG. 21

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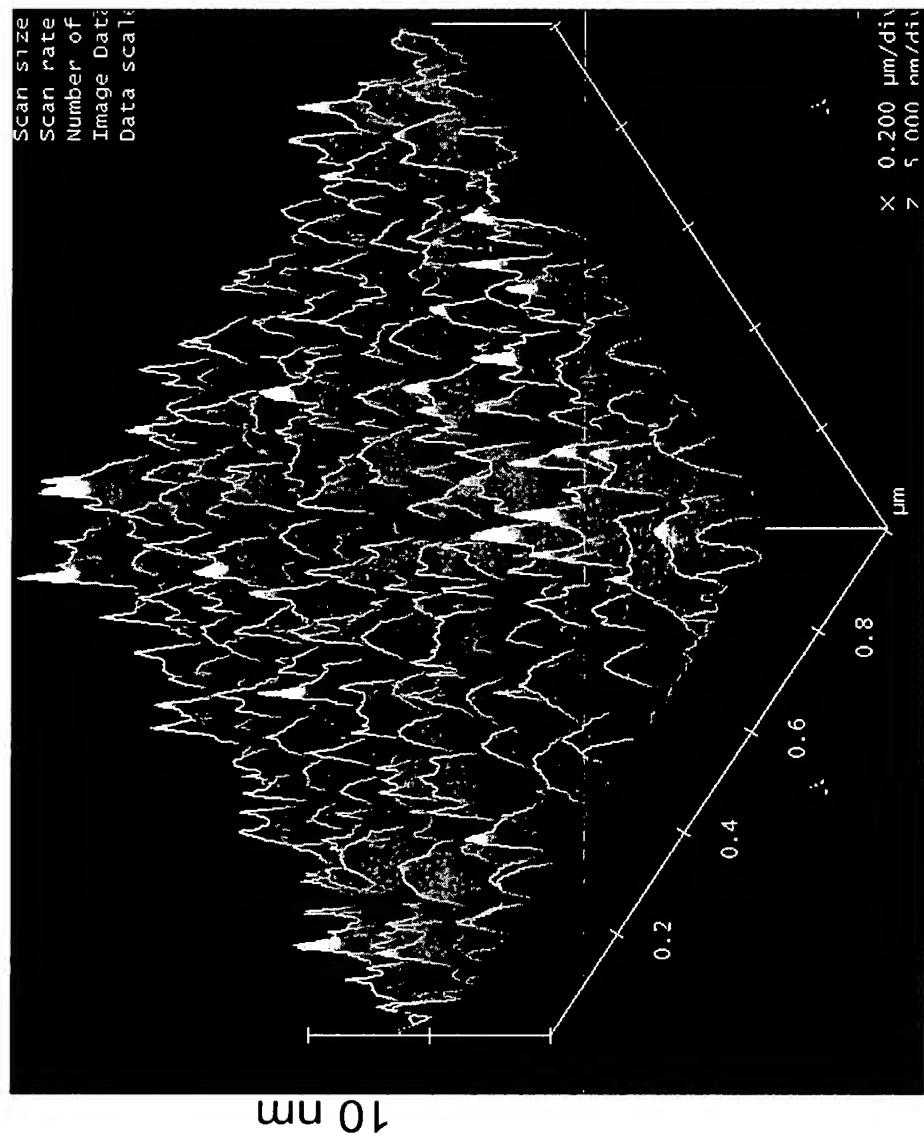


FIG. 22

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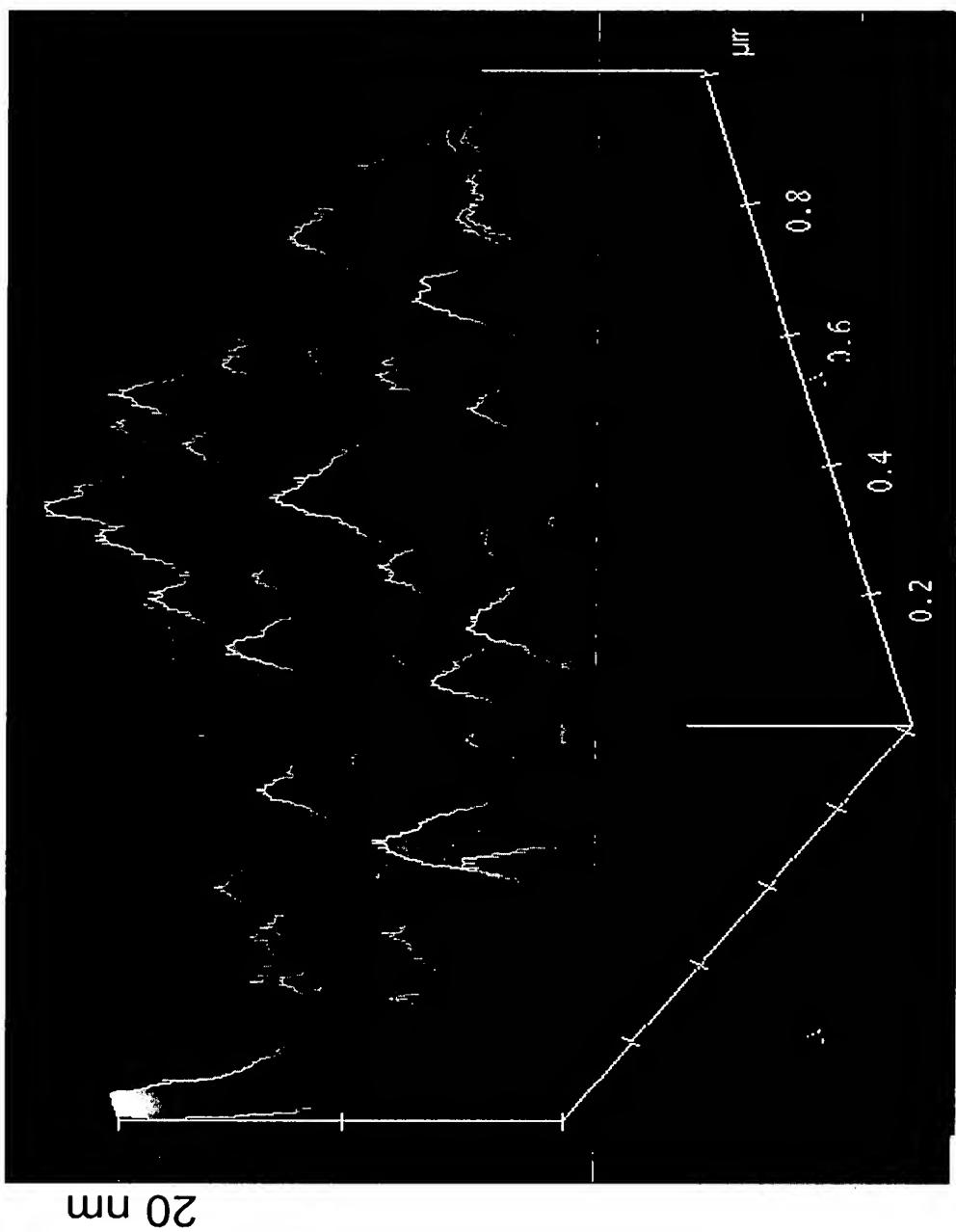


FIG. 23

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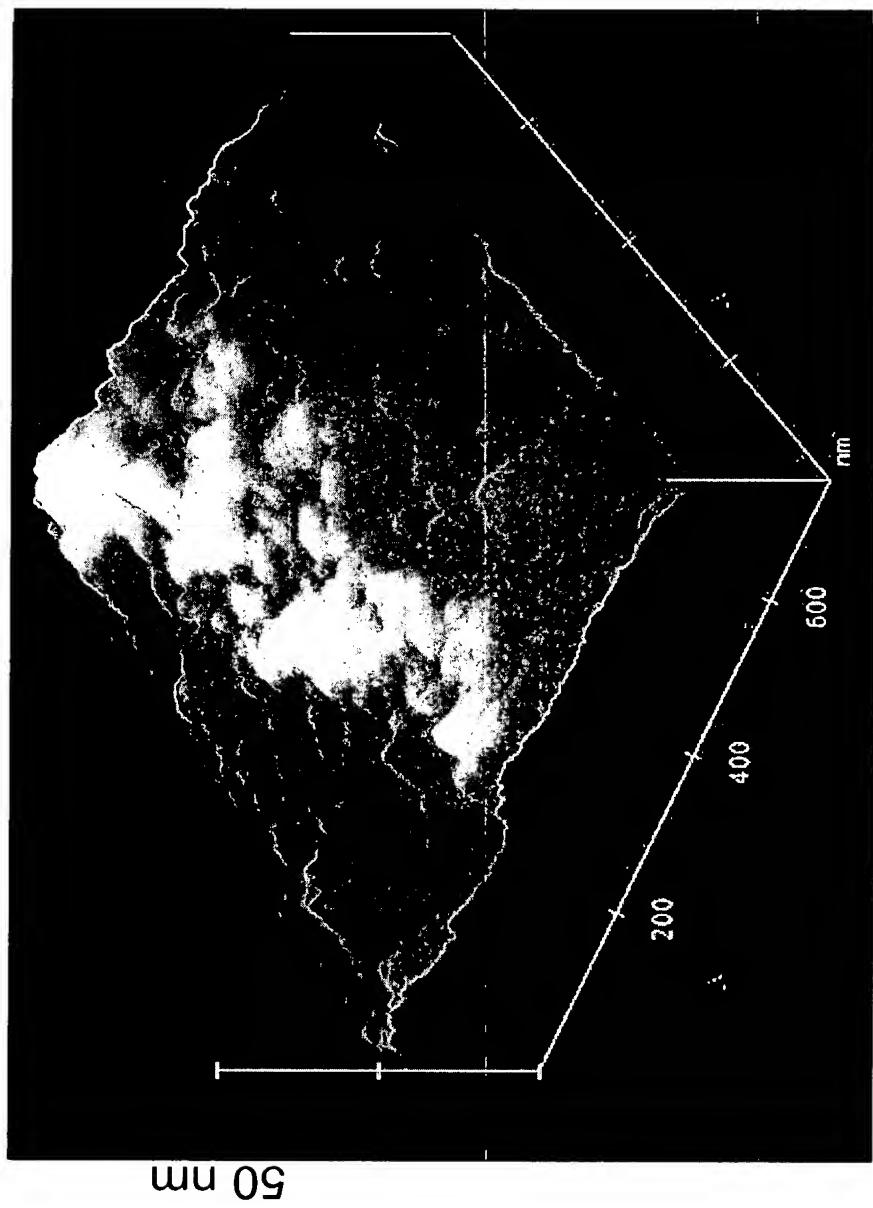


FIG. 24

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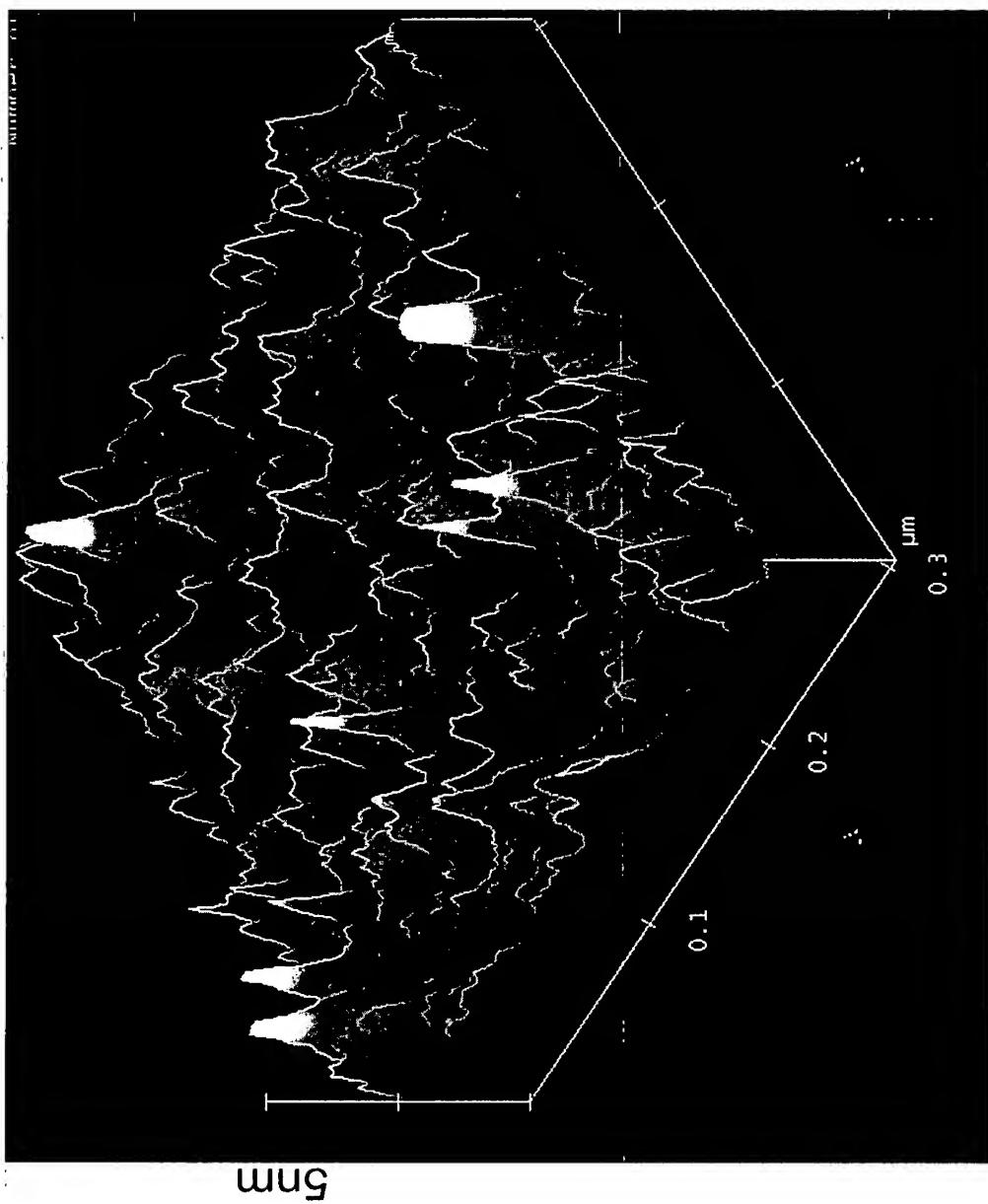


FIG. 25

DERWENT-ACC-NO: 2008-K07205

DERWENT-WEEK: 200859

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TITLE: Modifying surface of polymeric, inorganic, dendritic, or vinyl-functionalized substrate by plasma-induced graft polymerization, comprises cleaning substrate and then conditioning in humidity chamber, and treating the substrate with plasma

INVENTOR: COHEN Y; LEWIS G T

PATENT-ASSIGNEE: UNIV CALIFORNIA [REGC]

PRIORITY-DATA: 2006US-857874P (November 10, 2006)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE
WO 2008060522 A2	May 22, 2008	EN
WO 2008060522 A3	July 10, 2008	EN

DESIGNATED-STATES: AE AG AL AM AT AU AZ BA BB BG BH BR BW BY BZ CA CH CN CO CR CU CZ DE DK DM DO DZ EC EE EG ES FI GB GD GE GH GM GT HN HR HU ID IL IN IS JP KE KG KM KN KP KR KZ LA LC LK LR LS LT LU LY MA MD ME MG MK MN MW MX MY M Z NA NG NI NO NZ OM PG PH PL PT RO RS RU SC SD SE SG SK SL SM SV SY TJ TM TN TR TT TZ UA UG US UZ VC VN ZA ZM ZW AT BE BG BW CH CY CZ DE DK EA EE ES FI FR GB GH GM GR HU IE IS IT KE LS LT LU LV MC MT MW MZ NA NL OA PL PT RO SD SE SI SK SL SZ TR TZ UG ZM

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 LT LU LY MA MD ME MG MK MN MW MX MY
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 IT KE LS LT LU LV MC MT MW MZ NA NL
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APPLICATION-DATA:

PUB-NO	APPL- DESCRIPTOR	APPL-NO	APPL-DATE
WO2008060522A2	N/A	2007WO- US023785	November 13, 2007

INT-CL-CURRENT:

TYPE	IPC DATE
CIPP	B05D1/04 20060101
CIPP	H01M8/10 20060101
CIPS	C08J5/20 20060101
CIPS	C08L9/00 20060101

ABSTRACTED-PUB-NO: WO 2008060522 A2

BASIC-ABSTRACT:

NOVELTY - The method for modifying a surface of a polymeric, inorganic, dendritic, or vinyl-

functionalized substrate by plasma-induced graft polymerization, comprises cleaning the substrate and then conditioning in a humidity chamber for a desired length of time, treating the substrate surface with an atmospheric pressure (AP) plasma and an ethylenically unsaturated monomer solution, forming active sites on the substrate surface by directing the AP plasma at the substrate, and forming graft polymers bound to the substrate surface by contacting the active sites with a monomer solution.

DESCRIPTION - The method for modifying a surface of a polymeric, inorganic, dendritic, or vinyl-functionalized substrate by plasma-induced graft polymerization, comprises cleaning the substrate and then conditioning in a humidity chamber for a desired length of time, treating the substrate surface with an atmospheric pressure (AP) plasma and an ethylenically unsaturated monomer solution, forming active sites on the substrate surface by directing the AP plasma at the substrate, and forming graft polymers bound to the substrate surface by contacting the active sites with a monomer solution. The substrate comprises a thiol/silylated layer and a Langmuir-Blodgett film. The inorganic substrate comprises an adsorbed polymeric layer, an inorganic oxide, a metallic or ceramic material capable of supporting formation of surface oxides, hydroxides, peroxides or other functional groups for initiating polymerization of an unsaturated monomer. The plasma treatment is carried out within 10 seconds and at a radio frequency power of 40 W using hydrogen plasma. The monomer solution (50 vol.%) includes a polar monomer and a polar solvent, and has a low contact angle with the substrate to wet the surface of the substrate. The AP plasma is provided by a plasma jet, and formed from a precursor gas, which is carried by a carrier gas. The graft polymers are grown by free radical graft polymerization in the presence of a free-radical molecule, and have polydisperse chain lengths

with polydispersity index of less than or equal to 1.5. The plasma treatment time, radio frequency power, plasma source, plasma precursor gas, plasma carrier gas and/or applied voltage are adjusted to maximize the formation of surface initiation sites with respect to the amount of adsorbed water on the substrate surface. The plasma-treated substrate surface is contacted with the unsaturated monomer solution for a first time interval (t_1) at a first temperature (T_1) and for a second time interval (t_2) at a second temperature (T_2), where t_1 less than t_2 and T_1 greater than T_2 .

INDEPENDENT CLAIMS are included for:

- (1) a method of forming a polymer film and anchoring the polymer to a substrate; and
- (2) an inorganic or organic substrate.

USE - The method is useful for modifying a surface of a polymeric, inorganic, dendritic, or vinyl-functionalized substrate by plasma-induced graft polymerization (claimed).

ADVANTAGE - The method enables improved stability of the substrate surface by minimizing the polydisperse chain growth on the surface, and provides a high-density surface activation and graft polymerization without any extensive chemical surface treatment.

DESCRIPTION OF DRAWING(S) - The figure shows a schematic view of a method of modifying the silicon substrate.

EQUIVALENT-ABSTRACTS:

INORGANIC CHEMISTRY

Preferred Components: The inorganic substrate comprises an elemental material of silicon, aluminum, hafnium, zirconium, titanium, iron, gold and a silicon wafer. The inorganic oxide is silica, alumina, hafnia,

zirconia, and titania. The precursor gas is hydrogen, oxygen, nitrogen, air, ammonia, argon, helium, carbon dioxide and/or water.

ORGANIC CHEMISTRY

Preferred Components: The precursor gas is methane, ethane, propane and/or butane. The solvent of monomer is N-methyl pyrrolidone and/or water. The free-radical molecule comprises 2,2,6,6 tetramethylpipridine-1-oxyl (TEMPO) free-radical molecules.

POLYMERS

Preferred Components: The ethylenically unsaturated monomer comprises a vinyl or divinyl monomer having acrylic acid or methacrylic acid, an acid vinyl monomer, acrylic or methacrylic ester, polar vinyl monomer, non-polar vinyl monomer and 1-vinyl-2-pyrrolidone or styrene. The organic polymer is polystyrene, polyamides, and polysulfones.

CHOSEN-DRAWING: Dwg.1/25

TITLE-TERMS: MODIFIED SURFACE POLYMERISE INORGANIC DENDRITE VINYL FUNCTION SUBSTRATE PLASMA INDUCE GRAFT COMPRISE CLEAN CONDITION HUMIDITY CHAMBER TREAT

DERWENT-CLASS: A13 A14 P42 V05

CPI-CODES: A04-H00H; A10-C03A; A11-C04E; A12-S06A;

EPI-CODES: V05-F04; V05-F05C; V05-F05E3; V05-F05E5; V05-F08E;

ENHANCED-POLYMER-INDEXING: Polymer Index [1.1] 2004 ;
G0635 G0022 D01 D12 D10 D23
D22 D31 D41 D51 D53 D58 D75
D86 F71 H0146; G0282 G0271
G0260 G0022 D01 D12 D10 D26
D51 D53 D58 D60 D83 F36 F35
H0146 R00446 1911; G0306
G0271 G0260 G0022 D01 D12
D10 D26 D51 D53 D58 D60 D84
F36 F35 H0146 R00460 10151;
G0102 G0022 D01 D02 D12 D10
D19 D18 D31 D51 D53 D58 D76
D88 H0146 R00708 368; H0088
H0011; P1490*R F61 D01;
S9999 S1285*R; P1741;
P0088;

Polymer Index [1.2] 2004 ;
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Polymer Index [1.3] 2004 ;
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Polymer Index [1.4] 2004 ;
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Polymer Index [1.13] 2004 ;
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N7023; B9999 B5492 B5403
B5276; B9999 B5118 B5107

B4977 B4740;

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G2335 D00 F20 H* O* 6A
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SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: 2008-277042

Non-CPI Secondary Accession Numbers: 2008-731282